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Tin sulphide prepared by sulphurisation process using metallic tin film precursor obtained from dc magnetron sputtering method

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Abstract. Thin films of tin sulphide were prepared by sulphurisation process of metallic Sn precursor at temperature of 300-500°C in excess ambient of sulphur using a graphite box in N₂ atmosphere. Sulphurisation temperature at 300°C, the films were formed in SnS phase with orthorhombic structure. In contrast, the films were formed in SnS₂ phase with hexagonal structure when sulphurisation temperature higher than 300°C. From absorption spectra, direct band gap increased from 1.70 to 2.45 eV with increasing sulphurisation temperature. From the transient photoconductivity measurements, persistent photoconductivity behavior was observed in the films sulphurised at 300 and 350°C. The decay current data are better fitted with multiple exponential function resulting in the several slow decay times. Density of trap states corresponding to its decay time was also evaluated from the decay current data.

1. Introduction

In the past years thin films of SnS as a semiconductor of IV-VI group have attracted much attention because of their potential applications in the fabrications of photovoltaics, solar cells and optoelectronic devices [1]. Different values of band gap have been obtained for SnS, ranging from 1 to 2.33 eV [2], depending on the resulting structure obtained by different techniques and the type of electron transitions. In addition, both Sn and S are abundant in nature and non-toxic. The Sn-S system has three stoichiometric stable compounds, with variable Sn to S ratio such as SnS, SnS₂ and Sn₂S₃. Particularly, SnS shows the direct optical transition with p-type electrical conductivity. While SnS₂ found in polycrystalline nature with n-type conductivity and the compound Sn₂S₃ shows mixed valence compound with semiconductor nature. SnS₂ has CdI₂-like crystal structure that consists of densely packed atomic layers of tin located between two layers of S. This compound can exist in the form of several polytypes. The band gap of SnS₂ changes in the range of 2.12-2.44 eV depending on the method of desired materials and polytype. SnS₂ has n-type conductivity, a high optical absorption coefficient $> 10^4 \text{cm}^{-1}$ and relatively high charge carrier mobility $18.3\text{-}230 \text{cm}^2\text{V}^{-1} \text{s}^{-1}$. These properties make it promising for use in thin film solar cells. Tin sulphide films can be prepared by a variety of methods [2] with the purpose of manufacturing thin films suitable for use as a solar absorber in optoelectronic devices and photovoltaic applications. Among these methods, sulphurisation of Sn layers process is proposed low consumed materials, high growth rate, ease to control stoichiometric composition and ease to extend to large scale production. In this study, we prepared tin sulphide thin



films on glass slide substrates by sulphurisation process of metallic Sn precursor at temperature of 300-500°C in excess ambient of S using a graphite box in N₂ atmosphere. Influence of sulphurisation temperature on structural, optical and electrical properties of tin sulphide films was investigated.

2. Materials and methods

The Sn precursor layers were deposited on glass substrates using dc magnetron sputtering from a home-made circular planar magnetron sputtering system. A circular planar magnetron of 50 mm diameter was used as the magnetron cathode. The magnetron target assembly was mounted on the top plate of the sputter chamber such that the sputtering could be done by sputtering down configuration. A continuously variable dc power supply of 630 V and 2.6 A was used as a power source for sputtering. A 50 mm diameter and 3 mm thick pure Sn (99.99%) used as sputter target. Pure argon was used as sputter gas. The flow rate of argon was controlled by AALBORG mass flow controller. Before deposition of each batch, the target was sputtered in pure argon atmosphere for 5 min to remove oxide layer contaminated on the surface of target. The sputtered Sn layers were sulphurised in a graphite box kept in tubular furnace together with 99.98 % purity of S flakes (Sigma Aldrich) in N₂ flow. Sulphurisation temperature (T_s) was varied from 300 to 500°C for a fixed time period of 60 min and then the films were allowed to cool down naturally to room temperature. The crystal structure of these films was checked by X-ray diffraction technique with a Bruker D 8 diffractometer using CuK_α radiation. The crystallite size (L) was calculated using Scherrer's formula, neglecting peak broadening due to residual stresses in the films, $L = 0.9\lambda/(\beta\cos\theta)$ where β is the broadening of diffraction line measured at half its maximum intensity in radian and λ is the wavelength of X-rays (0.1540 nm). Surface morphology was examined by LEO1455VP scanning electron microscope. Optical absorption measurements were performed with UV-VIS double beam spectrophotometer in the wavelength range of 300- 800 nm. Electrical properties of the films were evaluated by Hall effect and resistivity measurements in the van der Pauw configuration at room temperature.

3. Results and discussion

3.1 Structural properties

The XRD patterns of tin sulphide films prepared at different sulphurisation temperatures are shown in Figure 1. The diffraction patterns with 2θ in the range of 20-70° showed that the films sulphurised at 300°C are polycrystalline in nature, exhibited several peaks corresponding to orthorhombic SnS phase with file JCPDS 39-354. The evidence of other phase such as Sn₂S₃ cannot be observed probably due to its peaks is weak intensity. In contrast, XRD spectrum of the films sulphurised at 350°C showed the well-defined peaks at 2θ equal to 28.20, 32.08, 49.90 and 52.42° well matched the standard patterns JCPDS 40-1467 with the hexagonal SnS₂ phase and corresponded to crystallographic planes (100), (101), (110) and (111), respectively. The variation of lattice parameter "a" and "c" of hexagonal SnS₂ phase as a function of sulphurisation temperature are shown in Figure 2. The calculated values of crystallite size using Scherrer's formula are 30.12, 42.36, 48.28, 49.77 and 59.01 nm for the films sulphurised at 300, 350, 400, 450 and 500°C, respectively. SEM images of tin sulphide films obtained from different sulphurisation temperatures are shown in Figure 3. It can be observed that the film surface sulphurised at 300°C was uniform with tightly packed particles. On further increase of sulphurisation temperature to 350°C, SEM image revealed many hexagonal thin plates of one side about 0.8 μm. These films had the thin plate shape with random orientation because SnS₂ was a layered compound semiconductor with CdI₂ structure [3]. When sulphurisation temperature increased from 350 to 500°C, the side of hexagonal plates rapidly increased from 0.8 to 2 μm whereas the thickness slightly increased. It is worthwhile to note that the crystallite size calculated by Scherrer's formula well corresponds to the thickness of the SnS₂ films observed by SEM images.

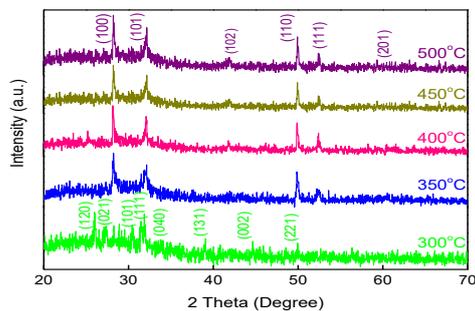


Figure 1. XRD patterns of Sn-S films as a function of sulphurisation temperature.

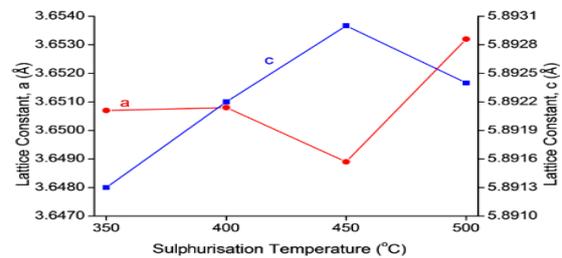


Figure 2. Lattice constants of SnS₂ films sulphurised between 350 and 500 °C.

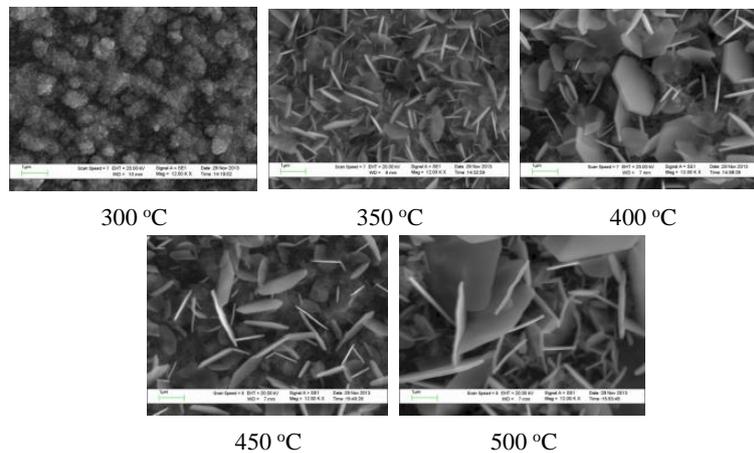


Figure 3. SEM images of Sn-S films sulphurised between 300 and 500°C.

3.2 Optical properties

Figure 4 shows absorbance spectra of tin sulphide films obtained from five sulphurisation temperatures during 300-500°C. From the absorbance spectra, the absorption coefficient (α) was calculated using the equation $\alpha = 2.303A/d$ where A is absorbance and d is film thickness. The absorption coefficient (α) and the incident photon energy ($h\nu$) related by $(\alpha h\nu)^2 = B(h\nu - E_g)$ where B and E_g are constant and band gap values, respectively. The E_g can be determined by extrapolation of the linear portion of the curve to the photon energy axis. Figure 5 shows the curve of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) of the films obtained from five different sulphurisation temperatures. The direct band gap type was clearly observed for all films sulphurised with different temperatures. The variation of E_g as a function of sulphurisation temperature is shown in Figure 6. The E_g increased from 1.70 to 2.45 eV with the increase of sulphurisation temperature from 300 to 500°C, respectively. The band gap (E_g) values of 1.38 eV for SnS phase and of 2.21 eV for SnS₂ phase were recently reported [4]. The difference in E_g values was mainly due to the difference in the deposition techniques employed and process parameters maintained during the growth of the films. The results indicated that E_g is sensitive to the sulphurisation temperature.

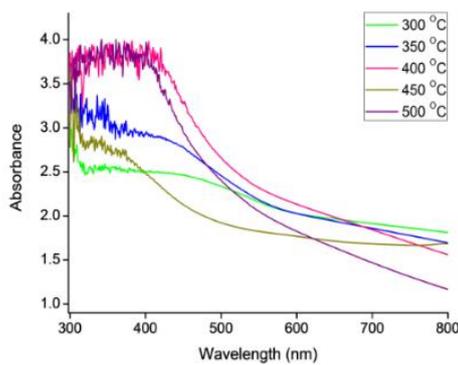


Figure 4. Absorbance of Sn-S films sulphurised between 300 and 500°C.

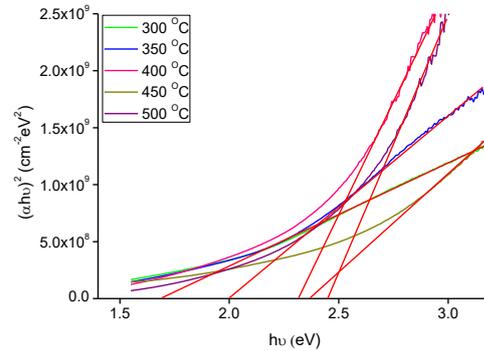


Figure 5. $(\alpha h\nu)^2$ vs. $h\nu$ plot of Sn-S films sulphurised between 300 and 500°C.

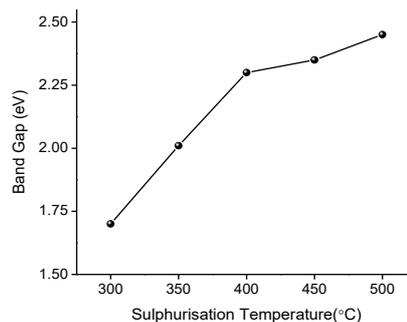


Figure 6. Variation of E_g of Sn-S films sulphurised between 300 and 500°C.

3.3 Electrical properties

Electrical properties of tin sulphide films were evaluated by Hall effect and resistivity measurements in the van der Pauw configuration. We found that the films sulphurised at 300°C exhibited p-type. In contrast, the films sulphurised at higher temperature ($> 300^\circ\text{C}$) converted to n-type conductivity. Carrier concentration (n) was derived from the relation $n=1/qR_H$ where R_H is the Hall coefficient and q is the absolute value of the electron charge. The carrier mobility (μ) was determined using the relation $\mu = 1/qn\rho$ where ρ is resistivity. Resistivity of the films increased from 6.42×10^2 to $1.24 \times 10^3 \Omega \cdot \text{cm}$ with an increase of sulphurisation temperature from 300 to 350°C. Further increase of sulphurisation temperature, resistivity sharply increased more than 2 orders ($> 10^9 \Omega \cdot \text{cm}$). It is consistent to the sudden increase of E_g from 2.01 to 2.30 eV when the sulphurisation temperature increased from 350 to 400°C. The carrier concentration decreased from 1.02×10^{16} to $2.72 \times 10^{14} \text{ cm}^{-3}$ when the sulphurisation temperature increased from 300 to 350°C. However, large increase in mobility value from 0.96 to $18.24 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when the sulphurisation temperature increased from 300 to 350°C was observed. Further increase of sulphurisation temperature, carrier concentration and mobility values cannot be obtained due to the films have very high resistivity values. The results indicate that the resistivity, carrier concentration and mobility of the films are sensitive to sulphurisation temperature.

3.4 Persistent Photoconductivity

The photocurrent response of the films sulphurised at 300 and 350°C was measured by two probe method using halogen lamp as a light source. Two silver electrodes were made on the sample surface. The photocurrent response of the films sulphurised at 300 and 350°C are shown in Figure 7. The sample was connected to the experimental setup and maintained in darkness under a constant applied bias of 30 V to stabilise the current. After the stabilisation period, the current was recorded in the following sequences: 30 s in darkness, 60 s under illumination and, finally, 90 s in the darkness. Under illumination, the current increased immediately because a lot of carriers were excited by light illumination. After the illumination period, the persistent photoconductivity (PPC) effect of the films sulphurised at 300 and 350°C occurred in darkness. The decay of PPC in Figure 7 can be described by multiple exponential functions [5] as equation (1).

$$I = I_{dark} + (I_0 - I_{dark}) \sum_i \exp\left(-\frac{t}{\tau_i}\right) \quad (1)$$

where I_{dark} is the current measured in darkness, I_0 is the PPC buildup level near the moment of light excitation being removed, τ is the PPC decay time constant. The normalised decay current in darkness as shown in Figure 8, which follows the illumination period, indicates the persistent of charge carrier traps in the films [5]. In Figure 8 the dash line is the measured data and the solid line is the least squares fit data by the multiple exponential functions as described above. Method for calculating the trap densities corresponding to the PPC decay constant was reported in the literature [6]. The decay time and density of trap states of the films sulphurised at 300 and 350°C were tabulated in Table 1. Our first decay time value in SnS phase is comparable to the previous reports [4,5] in which photoresponse times of about 20 to 40 s. The results suggested that the SnS films displayed shorter decay time values but slightly bigger density of trap states than SnS₂ films.

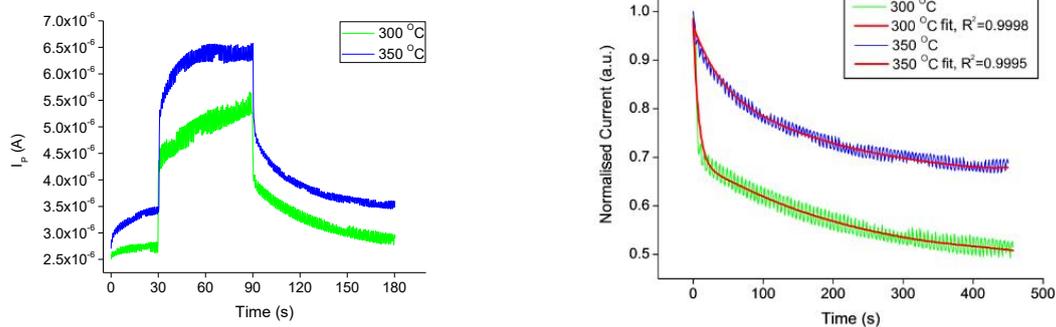


Figure 7. Photocurrent response of Sn-S films sulphurised at 300 and 350°C. **Figure 8.** Decay time of Sn-S films sulphurised at 300 and 350°C.

Table 1. Decay time and density of trap states of Sn-S films sulphurised at 300 and 350°C.

Sulphurisation temperature (°C)	Phase	Decay time (s)	Density of trap states ($\times 10^{10} \text{ cm}^{-2}$)
300	SnS	22.01, 534.75, 1076.35, 3211.02	2.29, 1.76, 1.66, 1.37
350	SnS ₂	114.02, 448.43, 632.91, 1276.77,	2.17, 2.03, 1.97, 1.82
		1352.64, 4856.33, 10162.65	1.71, 1.61, 1.54

4. Conclusion

Tin sulphide thin films were obtained through sulphurisation process of metallic Sn layers deposited on glass substrates by dc magnetron sputtering method. It is shown that the SnS single phase of orthorhombic structure was formed at sulphurisation temperature of 300°C whereas SnS₂ single phase was crystallised at sulphurisation temperature beyond 300°C. SnS films exhibited p-type but SnS₂ films showed n-type semiconductor. As the increase of sulphurisation temperature, band gap increased from 1.70 to 2.45 eV. From photocurrent response data, SnS films displayed shorter decay times but slightly bigger density of trap states than SnS₂ films.

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