

Influence of Annealing Temperature on tin Sulfide/ Silicon Photodiode Spectral Responsiveness

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Abstract : Thin film of Tin sulfide (SnS) have been deposited on glass substrates by means of thermal evaporation technique at two exceptional annealing temperatures 100 and 200 °C. (XRD) results confirmed that the crystalline dimension extended from (28 to 31) nm as the temperature of annealing increased, and this agrees with (SEM) and (AFM) results. The optical measurements verify that the energy reduce from about (2.45 to 2.30) electron volt with increasing the temperature of annealing due to Burstein–Moss effect. Al/SnS/n-Si/Al photodetector was fabricated and annealed at exceptional temperatures 100 and 200 °C in order to find out about the effect of annealing on the performance of the photodetector such as: the forward and reverse bias (I-V), capacity-voltage (C-V) characteristics, and responsivity. The outcomes confirm that the dark current in forward and reverse bias of Al/SnS/Si/Al photodetector improved with increasing annealing temperature, also the C-V characteristics showed that the built-in potential increased when the temp. of annealing increases and hence, the responsivity increased when the temperature of annealing increased and consequently the responsivity increased.

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I. Introduction

Optical sensors, a category of optical units that measure photovoltaic energy through converting falling light into currents or voltages, are extensively used as an essential part of spectroscopy, imaging, biological science and night vision [1–6]. Photovoltaic devices can almost be categorized as large-scale broadband or selective selectors, such as Si and InGaAs, which respond to energy-powered photons higher than their difference gaps [7,8]. Selective photodetectors, also known as narrowband photodetectors, are

designed to detect light at a specific wavelength and generally are applied for biomedical imaging and safety surveillance [9]. Both broadband and selective properties are required to build optical detectors which show a good optical response to a broad spectrum and are still spectrally distinctive. Tin sulfide thin films (SnS) have a great potential in solar cells due to their high absorption ($> 10^4 \text{cm}^{-1}$) and their conductivity [10]. Tin sulfide belongs to groups (IV and VI) compounds formed with Sn and S. SnS is an important optoelectronic material that is

found in zinc blende with lattice constant ($a=0.58 \text{ nm}$) [11], orthorhombic with lattice constants ($a = 0.385 \text{ nm}$, $b = 1.142 \text{ nm}$ $c = 0.43 \text{ nm}$) [12] crystal structures. The optical properties of SnS vary depending on the preparation process, but nearly all works agree with direct band gap (1.20–1.50) eV and indirect band gap (1.0– 1.20) eV values. These properties permit the use of SnS thin films as an absorption layer in the fabrication of heterojunction solar cells [13]. Tin sulfide thin films can be prepared by different methods such as thermal evaporation, pulse electrodeposition, SILR, electron-beam evaporation and chemical bath deposition [14–17]. In this article, the effect of annealing at 100 and 200 °C temperatures on SnS thin films and the performance of SnS-based Al/SnS/n-Si/A heterojunction photo-detector with Al electrodes has been investigated.

II. Experimental work

SnS thin films were deposited on glass and n-Si substrates by thermal evaporation with a rate of deposition is 40 nm/s at room temperature. The distance between the source and substrate was maintained at 6.5 cm; the film thickness was found to be about 100 nm. The samples were annealed at 100°C and 200°C for 2 hours in a high vacuum coating unit at a vacuum about $1.33 \times 10^{-2} \text{ Pa}$. XRD was used to study the structure and crystallinity of the deposited films. Scanning electron microscope (SEM) (T-scan Vega III Czech) and atomic force microscope (AFM) (AA 3000 scanning probe microscope) was employed to study the films morphology. SnS/Si heterojunction photodetector was fabricated by using aluminium as an ohmic contacts. For current-voltage measurements, a UNI-T-UT33C digital electrometer, (Tektronics CDM 250 multimeters and Laboratory compact

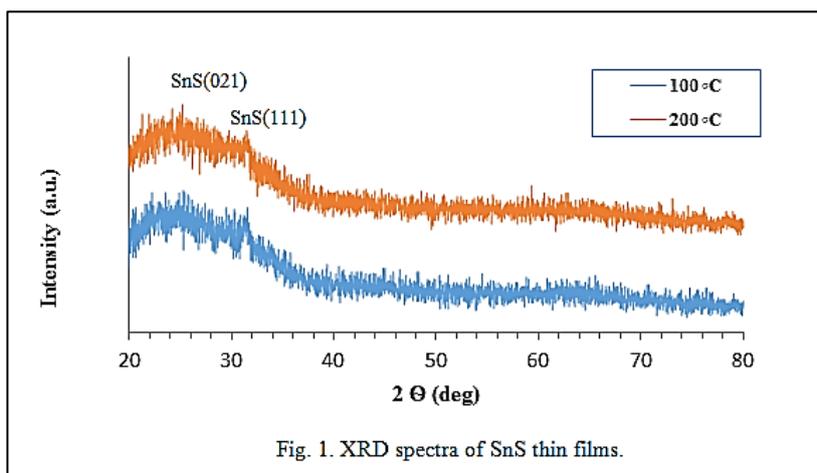
power supply unit) were used. Capacitance measurement as a function of reverse voltage (C-V) for Al/SnS/ Si/Al structure was carried out using LCZ meter at a frequency of 100 kHz. The measurement of the spectral responsivity was performed using a monochromator operating within the wavelength range of 400 to 900 nm.

1. Results and discussion

Fig. 1. Which indicates that the films have orthorhombic crystal structure are well compatible with the aforementioned structure [18,19]. Radiation diffraction peaks at angles of 26.14° and 32.12° corresponding to (021) and (111) planes, respectively. These peaks were in compliance with (JCPDS card 33-1375) standard values. From Fig.1, it is noticed that the peak intensity (021) increases with the temperature of annealing increases from 100 to 200°C. This confirms the dependence of crystallization on the annealing temperature. This observed growth in peak intensity is an evidence of the dependence of prepared samples crystallinity on annealing temperature. The film enhanced with increasing the temperature of annealing since the film exhibits better crystallinity and increased grain size, while the film heat-treated at the lower temperature of annealing exhibits poor crystallinity. The size of crystallite has been calculated using the Scherrer formula as in equation (1) [20] and it was found equal to 28 nm and 31 nm for the films annealed at 100 and 200 °C, respectively:

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

where: λ is the XRD wave-length in Å, β is FWHM in radian and θ is the diffraction angle of the XRD peak in degrees.



The investigation by SnS films showed that the tin and sulfur content in films varied gradually with annealing temperature. The annealed films maintained their initial stoichiometric composition of tin monosulphide. Annealing at 200 °C caused an increase in the tin fraction in the films, probably because more sulphur was lost during annealing at higher temperatures but at lower annealing temperature, the grown films were sulfur rich. Fig. 2 shows SEM images reveal granule growth, which is a multiple random-oriented distribution, and the growth of multi-twin grains pills randomly.

Through a microscopic image, the size of the granules is clearly increased by increasing the annealing temperature, this makes the films surface more homogeneous with better coverage and reduced porosity. The SEM images confirm the formation of well-defined SnS granules with a diameter of approximately 1 μm in the films annealed at 100 °C and approximately 10 μm for those annealed at 200 °C.

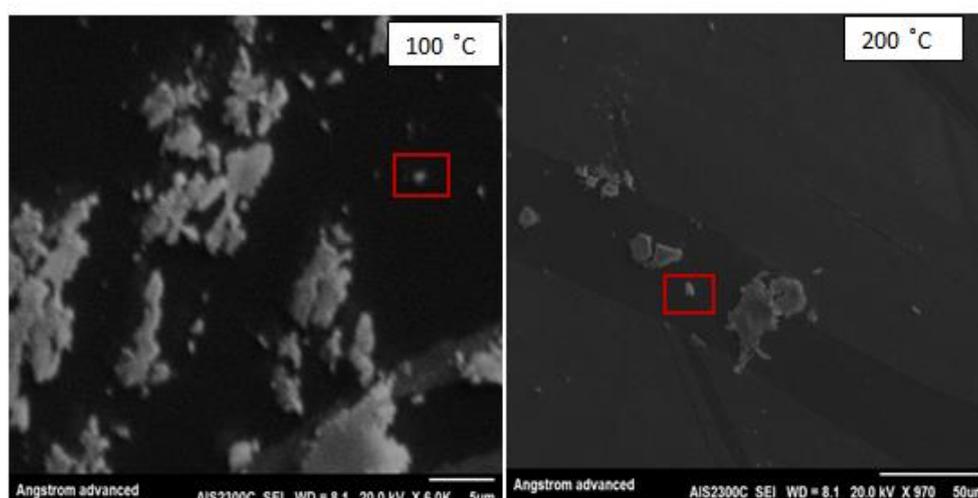


Fig. 2. SEM micrographs of SnS thin films annealed at 100 °C and 200 °C.

The sizes of the particles visible in the SEM images are much greater than the particle sizes measured by AFM due to agglomeration effect, as shown in Fig. 3. Two and three dimensional AFM images of the tin sulfide thin films that thermal annealed were shown in Fig.3. It was found that the average grains diameter and RMS values of surface roughness increase with increasing annealing temperature, which is in

consistent with SEM results. The variations of size of grain and surface roughness with annealing temperature are listed in Table 1. The average surface roughness was measured to be less than 5nm (1.24 and 2.14)nm. This reduces light reflection, but increases light absorption in the visible range of cells spectrum and photodetectors.

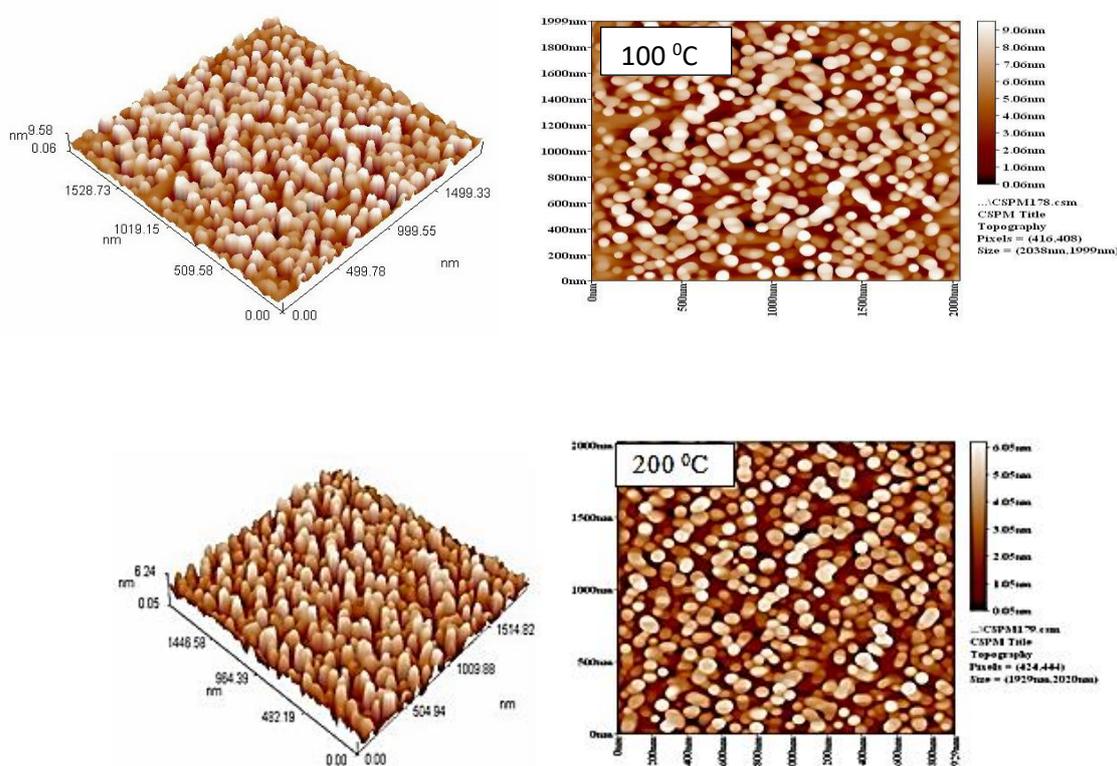


Fig. 3. 3D and 2DAFM images of SnS thin films annealed at (a)100°C and (b) 200°C.

Table 1: Average grain size, roughness average and RMS variation with annealing temperature.

Thermal annealing Ts [°C]	Average grain size [nm]	Roughness average [nm]	RMS [nm]
100	76	1.24	2.5
200	78	2.14	1.45

The optical energy gap for the SnS films has been investigated from the transmission spectra, with wave-length between 350 to 1100 nm. As shown in Fig. 4, films clearly have good transmittance characteristics and show a

decrease in absorbance after annealing at 100°C and 200°C, respectively. This is due to the growth in size of grain and the decrease in the number of faults. Fig. 5 shows the determination of the (E_g) of SnS thin films estimated from the

relation of $(\alpha h\nu)^2$ versus $h\nu$ plot (where α is the absorption coefficient). By extrapolating the linear portion of the curve to the photon energy axis, the energy gap value is found to be 2.39eV and 2.6eV at 100°C and 200°C, respectively. The increase in the value of E_g can be attributed

to the fluctuation of absorption edge, which is due to the energy band structure and the variation of density of state to the energy level. The poor crystallization of films may also increase the values of optical band gaps.

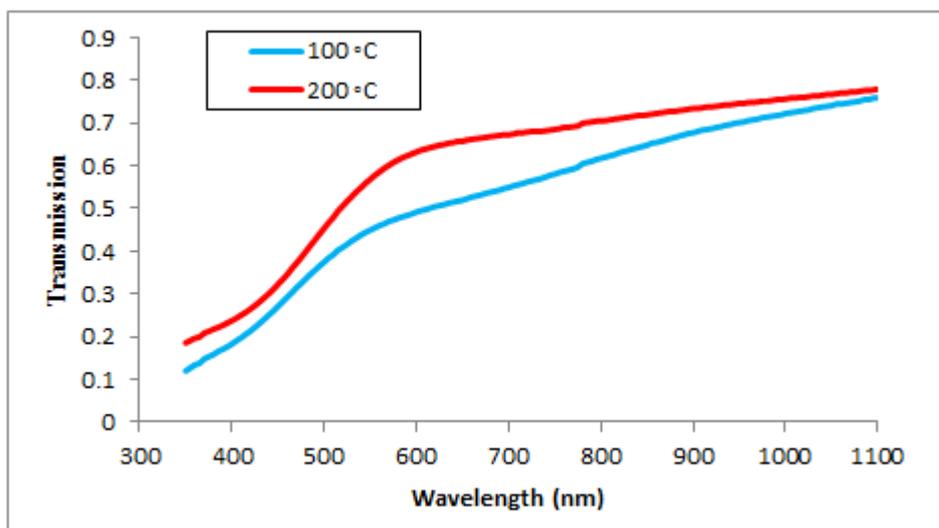


Fig. 4. Optical transmission of SnS thin films annealed at 100 and 200 °C.

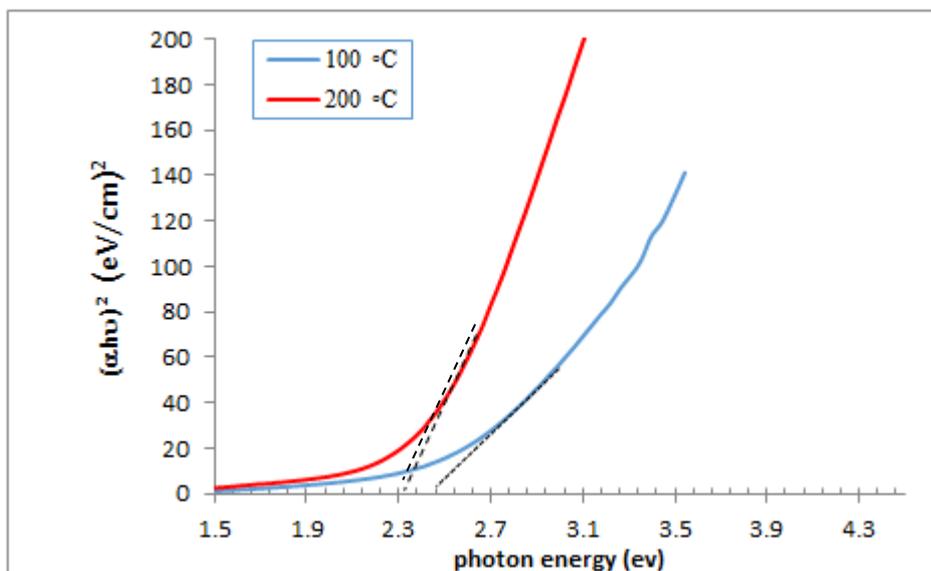


Fig. 5. Band gap determination of SnS thin films annealed at 100 and 200 °C.

Fig.6 illustrates the results obtained from the dark current-voltage (I-V) measurements in reverse and forward direction for the Al/SnS/

Si/Al photodetector. The figure shows that the dark current in the forward direction for the photodetector that was annealed at 200 oC is

four times higher than that of the photodetector annealed at 100 °C and this

attributed to decrease the energy gap after the annealing progress.

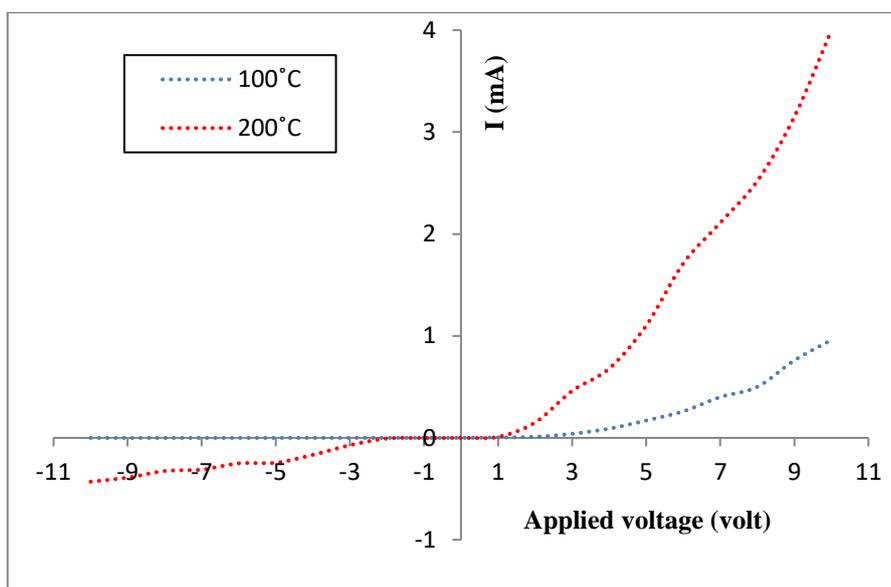


Fig.6.Dark I-V characteristics of Al/SnS/n-Si/Al photodetector heat-treated at different annealing temperatures.

$R(\lambda)$ Spectral responsivity is an important factor that determines the appropriateness of the detector signal for application [21]. Fig.7 shows the $R(\lambda)$ of Al/SnS/n-Si/Al photodetector annealed at 100°C and 200°C in the wave-length range of 400 –900nm under applying a bias voltage of 5 V, which is calculated by following equation [22,23] :

$$R_{(\lambda)} = \frac{I_{ph}}{P_{in}} \quad (2)$$

I_{ph} is the photocurrent and P_{in} is the input power. The figure shows that the optimum spectral responsivity value of 0.89A/W appears at 850nm at an temperature of annealing of 200°C.

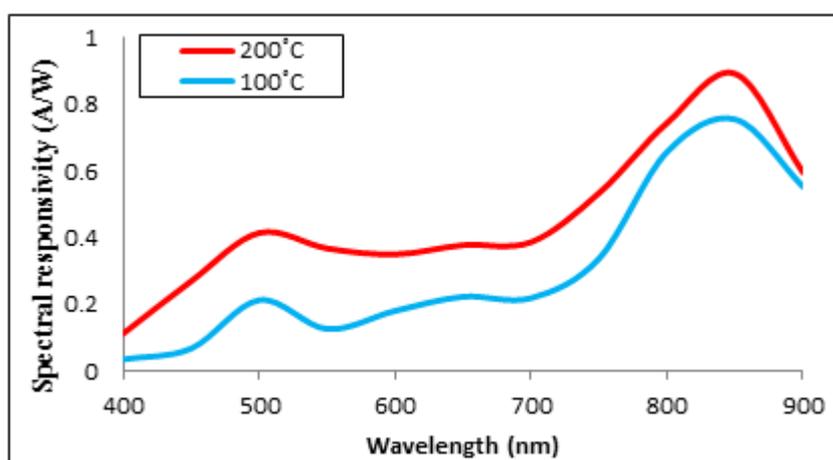


Fig.7: Spectral responsivity of SnS/ Si photo-detectors at different annealing temperatures.

The C-V measurement is useful to determine the type of the heterojunction (abrupt or graded), built-in potential (V_{bi}) which is the lowest energy required to cross the electron from SnS to n-Si (as in this work, the heterojunction is abrupt). From measuring the capacitance of (SnS/Si) for the annealed heterojunction with 100 °C and 200 °C, as a function of reverse bias, the value of V_{bi} can be found

from plots the relation between $1/C^2$ and reverse bias as shown in fig. 8. The intercept of a straight line with a voltage-built-in voltage axis (V_{bi}) was found to be about 0.8volts in order for plasticization heterojunction with 100 °C and 0.4 volts for steel with 200 °C, which means that the steel improves and heterojunction properties.

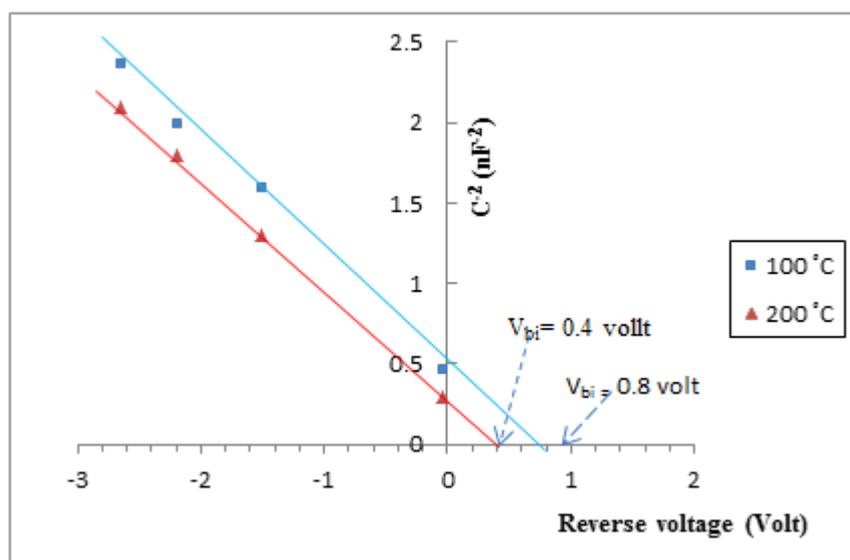


Fig. 8: $1/C^2$ versus reverse voltage of Al/SnS/ n-Si/Al Photo-detectors

4. Conclusions

The influence of temp. on the structural, morphological and optical properties of SnS thin films prepared by thermal evaporation had been investigated. The results of XRD indicated that the films had preferred (021) and (111) orientation. It was observed that the intensity of (021) peak becomes longer when temp. of annealing increased from 100 to 200°C. The temperature of annealing also impacted the morphological properties of the thin films, the surface roughness increased with increasing size of grains as the temperature of annealing increased. Current-voltage characteristics and spectral responsivity of Al/SnS/ Si/Al improved as the temperature of annealing increased

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