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# Crystal Structure, Optical, and Electrical Properties of SnSe and SnS Semiconductor Thin Films Prepared by Vacuum Evaporation Techniques for Solar Cell Applications

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**Abstract.** Thin films of SnSe and SnS semiconductors had been prepared by vacuum evaporation techniques. All prepared samples were characterized on their structure, optical, and electrical properties in order to know their application in technology. The crystal structure of SnSe and SnS was determined by X-Ray Diffraction (XRD) instrument. The morphology and chemical composition were obtained by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive of X-Ray Analysis (EDAX). The optical property such as band gap was determined by DR-UV-Vis (Diffuse Reflectance-Ultra Violet-Visible) spectroscopy, while the electrical properties were determined by measuring the conductivity by four probes method. The characterization results indicated that both SnSe and SnS thin films were polycrystalline. SnSe crystallized in an orthorhombic crystal system with the lattice parameters of  $a = 11.47 \text{ \AA}$ ,  $b = 4.152 \text{ \AA}$  and  $c = 4.439 \text{ \AA}$ , while SnS had an orthorhombic crystal system with lattice parameters of  $a = 4.317 \text{ \AA}$ ,  $b = 11.647 \text{ \AA}$  and  $c = 3.981 \text{ \AA}$ . Band gaps ( $E_g$ ) of SnSe and SnS were 1.63 eV and 1.35 eV, respectively. Chemical compositions of both thin films were non-stoichiometric. Molar ratio of Sn : S was close to ideal which was 1 : 0.96, while molar ratio of Sn : S was 1 : 0.84. The surface morphology described the arrangement of the grains on the surface of the thin film with sizes ranging from 0.2 to 0.5 microns. Color similarity on the surface of the SEM images proved a homogenous thin layer.

**Keywords:** Vacuum evaporation, solar cell, SnSe semiconductor, SnS semiconductor.

## 1. Introduction

The studies of semiconductor materials, i.e. tin monoselenide or monosulfide are mostly done by researchers because the materials are semiconductor materials that can be applied in several areas of technology. One of their applications is in solar cell technology, due to the band gap of both materials that falls in the photon energy range of the spectrum of solar cells [1]. The study of SnSe has been widely conducted by several researchers, for example, research related to the structure and optical properties of SnSe thin film obtained by Chemical Bath Deposition (CBD) [2]. Other researchers



obtained SnSe using Aqueous Solution Method [3], and had also been reported that SnSe thin film were prepared by photoelectrochemical techniques deposition [4]. Research on SnS thin film had also been successfully produced by spray pyrolysis method [5], electrodeposition technique [6] and of course with other techniques.

## 2. Experimental Procedure

### 2.1 Preparation of SnSe and SnS Semiconductors

At first, the vacuum system equipment consisting of a primary pump in the form of rotary van pump capable of suppressing the pressure up to  $10^{-3}$  Torr was prepared. The primary pump was connected to the secondary pump in the form of diffusion pumps which were capable of decreasing the pressure of evaporator chamber at  $10^{-6}$  Torr. Evaporator was equipped with boat-shaped crucible made of molybdenum (Mo) and connected to a power supply system that can generate electrical currents of up to 300 A. Crucible was mounted above the support where the substrates can be put and equipped with electrodes that can be connected to a power supply to set the substrate temperature.

SnSe powder was placed on the crucible, and then heated by slowly flowing current to crucible until the temperature reached above 1000 °C. The powder reached the point of vapor and deposited on the substrate at a temperature of 500 °C. After the deposition, the thin layers were left for 12 hours and then the evaporator was opened and a number of thin films were obtained. An equal treatment was done for the SnS powder.

### 2.2 Characterization

To determine the structures and parameters of the crystal lattice, the SnSe and SnS thin film were characterized by XRD. Both thin films were examined using powder X-ray diffraction (XRD). The XRD patterns were obtained on a Rigaku MiniFlex 600-Benchtop XRD instrument, operated in the Bragg configuration using Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). The XRD instrument ran at 40 kV and 15 mA. The intensities were determined in the  $2\theta$  interval ranging from 3° to 90°. The surface morphology and chemical composition of SnSe and SnS thin films were investigated by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Analysis of X-Ray (EDAX). To calculate the energy gap of the prepared samples, Diffuse Reflectance UV-Vis-UV 1700 Pharmaspec Spectroscopy at wavelengths ranged from 200 nm up to 900 nm was used. To specify the electrical properties such as conductivity and resistivity of the thin films, four-point probe technique was used.

## 3. Results and Discussion

SnSe and SnS thin films have been successfully obtained by vacuum evaporation techniques through the implementation of following variables variation. Variable control include vacuum pressure, the mass of material, and the temperature source (crucible) and the distance between the crucible and substrate, while the independent variables in this study were four variations of the temperature of the substrate, namely without heating, 250, 350, 500 and 550 °C [7]. In this article, only substrate temperature at 500 °C was reported to get the best values of the physical parameters after the characterization had been done. The characterization includes the structure and parameters of the crystal, the composition of the sample, optical properties and electrical properties of the thin film prepared using vacuum evaporation techniques.

### 3.1 XRD spectra of SnSe and SnS thin films

XRD (X-Ray Diffraction) can be used to determine the crystal lattice parameters and the structure of thin films. The data obtained from XRD analysis were in the form of a graph of intensity ( $I$ ) and the spectrum of diffraction angle ( $2\theta$ ). Diffractogram displays spectral peaks that appeared in the samples. XRD analysis showed the distance among the crystal planes  $hkl$  ( $d_{hkl}$ ). Diffraction patterns obtained from the sample were then compared with the data of JCPDS (Join Committee on Powder of Diffraction Standards) so it can be determined the Miller index from the diffraction peaks was formed.

The calculation of parameters can also be done once the crystal structure was known. Figure 1 shows the diffractogram of SnSe and SnS samples. The lattice parameters of orthorhombic crystal system can be calculated using the following equation [8].

$$2d \sin \theta = n\lambda$$

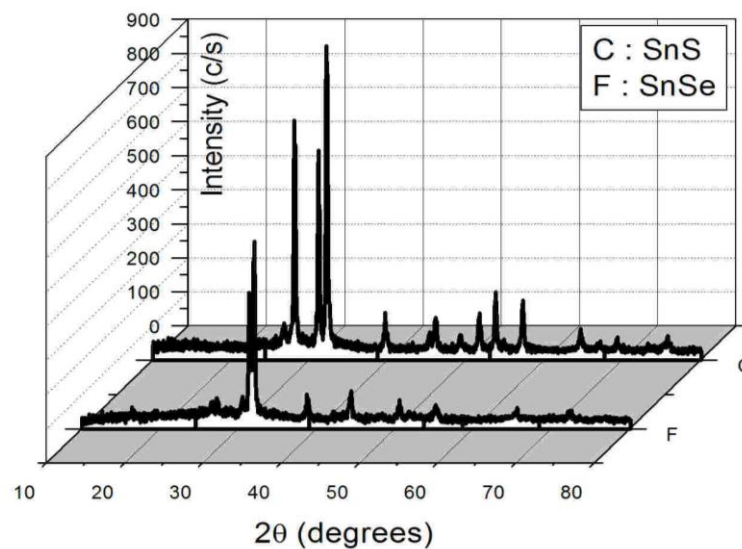
where  $d$  can be calculated by  $\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$ , so the following relationship can be applied:

$$\sin^2 \theta = \frac{\lambda^2}{4} \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)$$

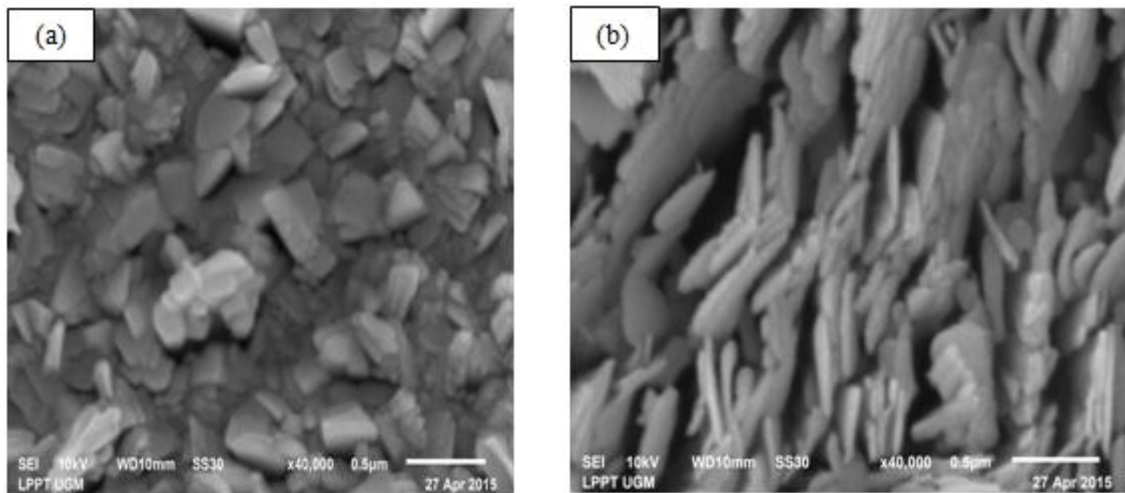
where  $d$  is the distance of crystal planes,  $\theta$  is the diffraction angle,  $\lambda$  is X-ray wavelengths,  $h k l$  is Miller Index, and  $a, b, c$  are the crystal lattice parameters. The calculation of each SnSe and SnS sample presented the crystal parameters of  $a= 11.47 \text{ \AA}$ ,  $b= 4.152 \text{ \AA}$  and  $c = 4.439 \text{ \AA}$  for SnSe, and  $a = 4.317 \text{ \AA}$ ,  $b = 11.647 \text{ \AA}$  and  $c = 3.981 \text{ \AA}$  for SnS. These results were consistent with other researchers' research findings [9,10].

### 3.2 SEM and EDAX

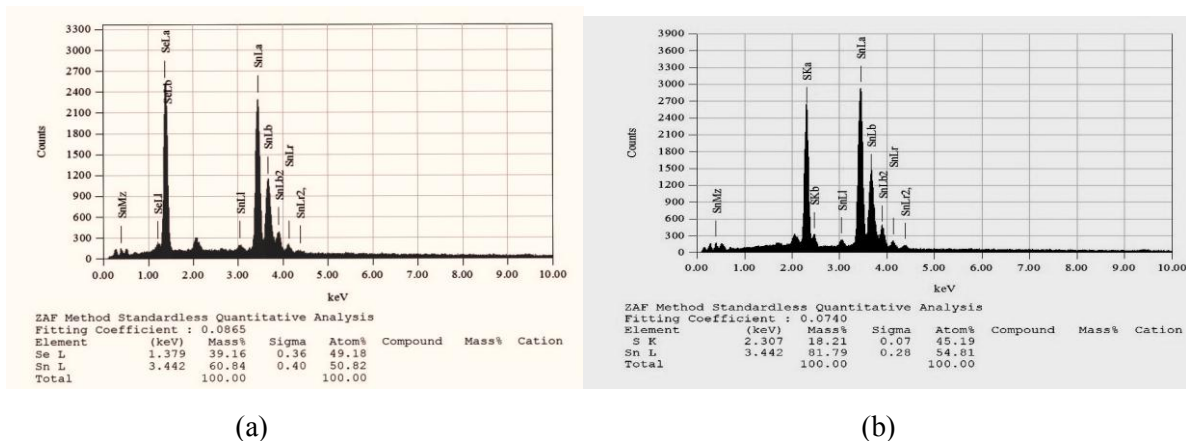
Scanning Electron Microscopy (SEM) is an instrument used to determine the morphology of the surface of a material. The morphology of the surface of SnSe and SnS thin films were obtained through capturing and processing the secondary electrons emitted by a thin film when subjected to electron beams. The results of SEM characterization were images that depicted the surface of a crystal. The surface morphology characterization of SnSe and SnS samples with 40,000 times magnification is shown in Figure 2.



**Figure 1.** Diffraction patterns of SnSe and SnS thin films



**Figure 2.** SEM images of (a) SnSe and (b) SnS thin films



**Figure 3.** EDAX on chemical compositions of (a) SnSe and (b) SnS samples

Based on the morphological images resulted from the characterization by SEM as in Figure 2, it appears that there is homogeneity of Se and S crystals in the thin film. The SEM images showed that the structures of the sample are in bead and angled beam shapes and scattered on a regular basis. The granular form according to orthorhombic crystal structure which has an axis perpendicular to each other and had one parameter longer compared with the two other lattice parameters. The chemical composition of the thin films analyzed by EDAX can be seen in Figure 3.

EDAX is integrated with SEM and it cannot work without SEM. Therefore, the EDAX was integrated with SEM device. The results of EDAX are in the form of aspectrum describing the relationship among the energy intensities resulting from firing electron beam on the sample. EDAX testing would produce two forms of analysis: qualitative and quantitative analyses. Qualitative analysis was used to calculate the type of element that was present in the sample where energy peaks appear on the curve being analyzed, whereas quantitative analysis was used to determine the composition of the constituent elements of the material being analyzed. From this quantitative analysis, the identification of elements completed with mass and atomic percentages are shown. The expected value of molar ratio of Sn and Se, also of Sn and S is 1 : 1. Based on EDAX characterization results, the SnSe and SnS thin films contained Tin (Sn), Selenium (Se) and sulfur (S). But the result was slightly deviate from expectations. The molar ratio of Sn and Se in SnSe was 51.03% : 48.97% or 1 : 0.96, and of Sn and S in SnS was 54.47% : 45.53% or 1:0.84.

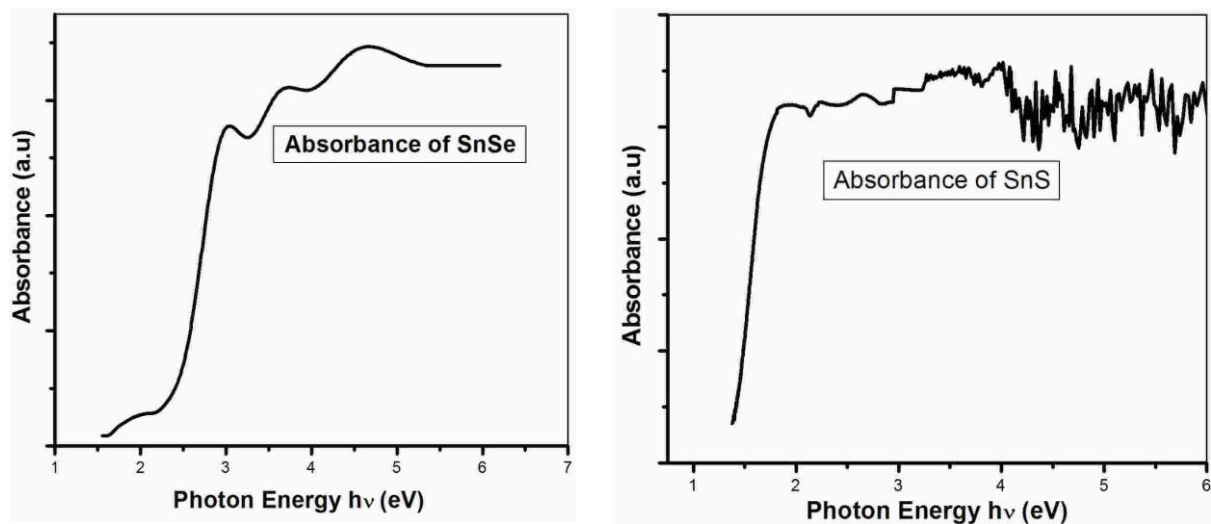
### 3.3 Optical and electrical properties

The sample characterization for optical properties was carried out by UV-VIS spectroscopy with a wavelength ranged from 200 nm up to 900 nm. This equipment was not perfect because it could not reach up to the NIR with a wavelength of about 4000 nm. However, specifically for SnSe and SnS materials, it can be used to show the band gap width of both materials in the wavelength range of the spectrum. The absorption of wavelength can occur when radiation passes through the band gap of the material.

The phenomenon arose when inside the energy is passed so that the absorbance is very small a band gap. When a photon of energy was equal to or greater than the band gap, the absorption will occur so that the absorbance ( $A$ ) would go up significantly. The absorbance spectrum as a function of photon energy can be shown in Figure 4.

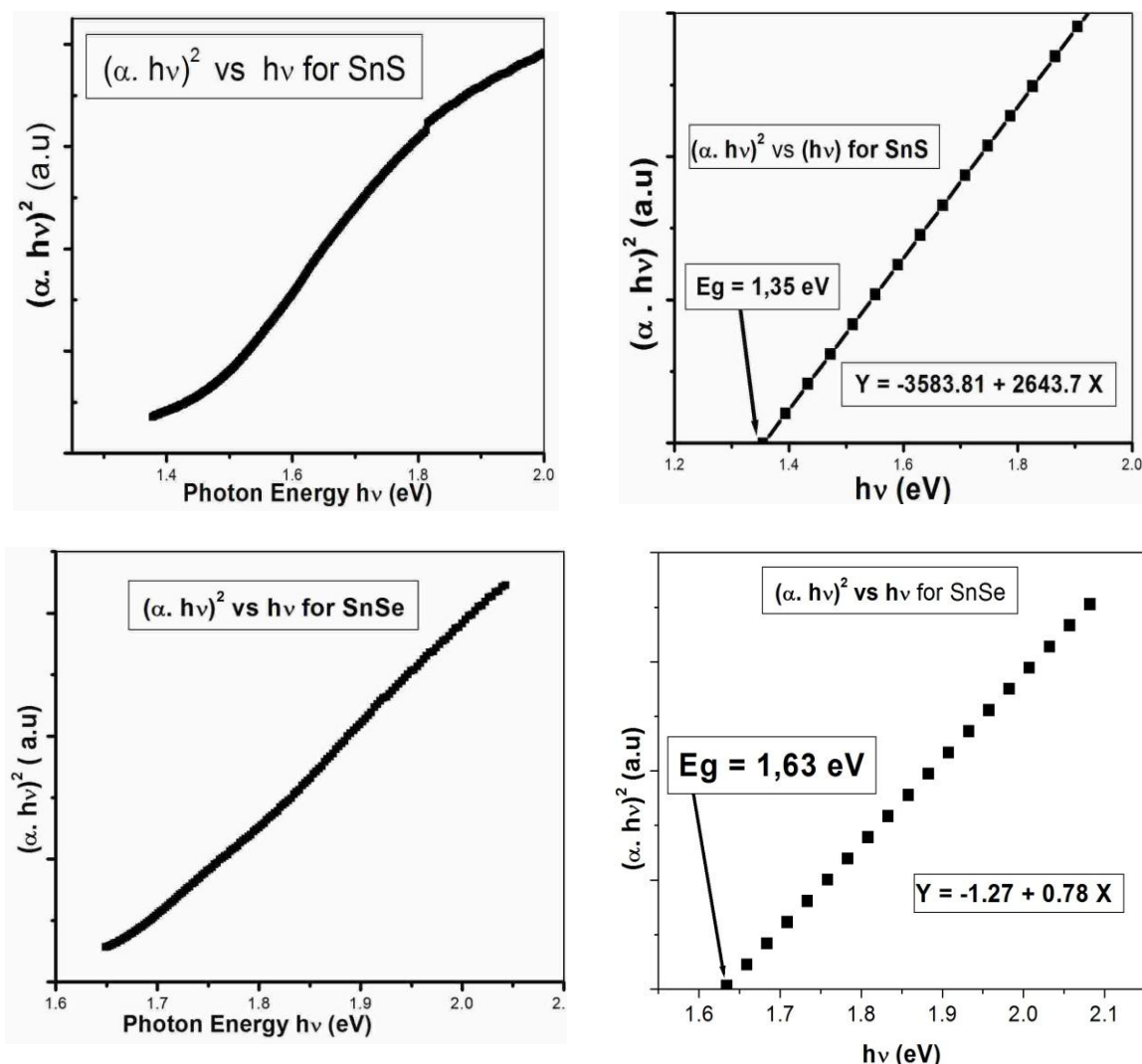
The calculation of the band gap of materials can be done using the formulation as follows. Absorption coefficient  $\alpha$  is proportional to the absorbance  $A$ , so it can be stated that  $\alpha = 2.303A/d$ , where  $d$  is the thickness of the thin films. Then the relationship between  $\alpha$  and the photon energy  $h\nu$  for direct band gap semiconductor material was given by the equation of  $(\alpha, h\nu)^2 = B^2(h\nu - E_g)$ , where  $B$  is a constant between  $10^5$  and  $10^6 \text{ cm}^{-1}\text{eV}^{-1}$  [11]. The result of this calculation produced the width of SnSe and SnS band gaps of 1.63 eV and 1.35 eV respectively. The results are consistent with the results obtained by other researchers [12,13].

The data, such as shown in Figure 4, can be processed to produce  $(\alpha, h\nu)^2$  as a function of photon energy  $h\nu$  as shown in Figure 5. Based on the measurement of electrical properties, it can be seen that all SnSe and SnS samples had the same conductivity type, which is p-type, with average specific resistivity of  $4.6 \times 10^{-2} \text{ ohm-cm}$  and  $4.4 \times 10^{-2} \text{ ohm-cm}$ , respectively. Both samples were prepared at the same substrate temperature which was  $500 \text{ }^\circ\text{C}$ . This result was in accordance with the range of resistance values of semiconductor materials.



**Figure 4.** The absorbance spectrum of SnSe and SnS as a function of photon energy





**Figure 5.**  $(\alpha \cdot hv)^2$  as a function of photon energy  $hv$  of SnS and SnSe thin layers

#### 4. Conclusion

SnSe and SnS semiconductor thin films had been successfully prepared by vacuum evaporation techniques. The thin films were composed of atoms in orthorhombic crystal structure with the lattice parameters of  $a = 11.47 \text{ \AA}$ ;  $b = 4.152 \text{ \AA}$  and  $c = 4.439 \text{ \AA}$  for SnSe, and  $a = 4.317 \text{ \AA}$ ,  $b = 11.647 \text{ \AA}$  and  $c = 3.981 \text{ \AA}$  for SnS. The observations from EDAX indicated that SnSe and SnS samples were both non-stoichiometric with molar ratio of Sn:Se = 1:0.96 and Sn:S = 1:0.84. Electrical and optical properties of SnSe and SnS indicated that both materials have p-type conductivity with an average of resistivity of  $4.6 \cdot 10^{-2} \text{ ohm-cm}$  and  $4.4 \cdot 10^{-2} \text{ ohm-cm}$  and with band gaps of ( $E_g$ ) of 1.63 eV and 1.35 eV, respectively.

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