



Optimization of Sn_xSe_y deposited by reactive thermal evaporation for solar cell application

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ABSTRACT

In this study, tin selenide was prepared at different ratios using tin and selenium pellets in glass tube filled with argon and then heated up to 350°C. The resulting materials were cut into ingots which were used in preparation of thin films by thermal evaporation. The evaporation was done using Edwards auto 306 coating unit. The chamber pressure was maintained at 5.0×10^{-5} mbars during the film deposition. Thin films of tin-selenide produced using various ratios were characterized for optical properties and sheet resistance. The optical measurements were done using UV-VIS-NIR spectrophotometer Solid State 3700 DUV in the visible range (380-750nm) and the transmittance spectra data obtained was analyzed using the SCOUT software. The films with ratio of 1:1 showed the highest transmittance of 85% with a band gap energy obtained as 1.40eV. The electrical characterization measurements were carried out using a four point probe at room temperature (25°C) to obtain the sheet resistivity. The resistivity obtained for the films was 20.1Ωcm.

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Introduction

Extensive attention has been paid in search of new semiconducting materials for efficient solar energy conversion. Group IV-VI offer a range of optical band gaps suitable for various optoelectronic applications such as memory switching devices, solar cells, holographic recording systems and gas sensors [1]. Tin selenide is direct band gap group IV-VI semiconductor with a melting point of 860°C and an energy gap of about 1 eV [2]. A number of techniques have been employed in the formation of high quality thin films such as Chemical Vapor Deposition, Molecular Beam Epitaxy, Electrochemical Atomic Layer Epitaxy, Thermal Evaporation and Sputtering [3]. However there is an interest to investigate other techniques, which could be new possibilities in terms of device properties and structure. Thermal Evaporation belongs to these alternative techniques that could also produce high quality films of IV-VI semiconductor materials [4]. It is an inexpensive, simple, low temperature method that could produce good quality films for device application. However the effect of the ratio of tin to selenium on the optical and electrical properties has not been investigated. In this study, thin films of tin selenide consisting of various ratios of tin to selenium were deposited by reactive thermal evaporation. The films were then characterized for the optical and electrical properties.

Materials and methods

Sample preparation

Tin selenide (Sn_xSe_y)

Tin selenide (Sn_xSe_y) compound was prepared from tin and selenium pellets. The purity given by the supplier was 99.9% for tin while that of selenium was 99.99%. The alloy was prepared by mixing tin and selenium in their specific ratios by mass as shown in Table 2.1 in a sealed glass tube containing argon gas and the mixture was heated to a temperature of 350°C. This is because tin selenide (Sn_xSe_y) can be formed by heating tin in contact with selenium either in vacuum or in inert atmosphere above 200°C [5]. The heating was continuous and gentle to

prevent the glass from breaking. During the melting the shaking was continuously done to ensure homogeneity. The temperature was measured using a thermocouple thermometer. The compound formed was allowed to cool naturally to room temperature (25°C) thus solidifying into an ingot. The setup that was used in preparation of the alloy ingots is shown in Figure 2.1.

Table 2.1. Tin selenide samples showing various tin to selenium ratios

Sample name	Sn:Se
A	1:0.2
B	1:0.4
C	1:0.6
D	1:0.8
E	1:1.0

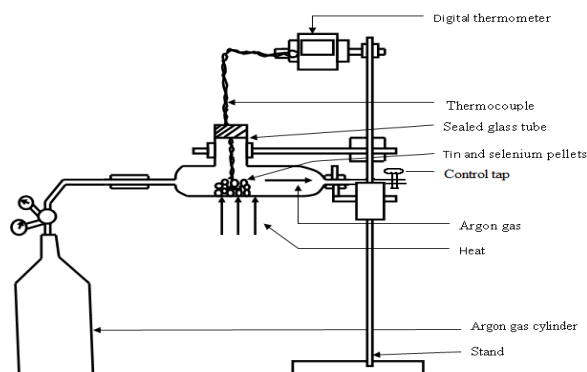


Figure 2.1 Setup used for melting tin and selenium to form tin selenide ingot

Five samples were prepared separately and then the glass tubes were sealed. The glass tubes were broken after they had cooled to room temperature and the ingots were removed. Then from each of the samples labeled A to E, 0.1 g was measured using an electronic balance and placed in a boat for evaporation.

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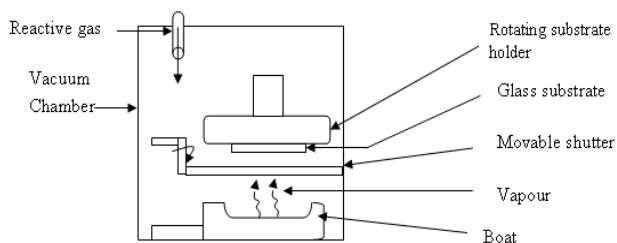


Figure 2.2: Vacuum evaporation chamber.

Thermal Evaporation

The deposition of the compound material was done using an Edwards auto 306 coating unit. The current was maintained at a constant value of 3.5A for 3 minutes for all the samples. This ensured that the deposition rate was maintained at 0.2 nm/sec for a uniform film thickness. Clean microscope glass slides were used as substrate. The glass slides were washed using a mixture of deionized water, liquid detergent and sodium hydroxide in the ratio of 3:2:1 and then dried with a spray of pressurized argon. A typical diagram of the vacuum evaporation chamber is shown in Figure 2.2.

Optical properties of tin selenide

The raw data for the optical transmittance of the deposited tin selenide thin films was measured using UV-vis-NIR spectrophotometer solid spec 3700 DUV at normal incidence. The data for each of the films was analyzed using the SCOUT software and the respective graphs plotted using originPRO7 software.

Electrical characterization

The sheet resistance was carried out using the four point configuration at room temperature (25°C). The four point probe set up usually consists of four equally spaced tungsten metal tips with finite radius. Each tip is supported by springs on the other end to minimize sample damage during probing. The four metal tips are part of an auto-mechanical stage which travels up and down during measurements. A high impedance current source was used to supply current through the outer two probes and a voltmeter used to measure the voltage across the inner two probes as shown in figure 2.3. These values of sourced current and measured voltage were used to determine the sample resistivity. Typical probe spacing S was about 1 mm.

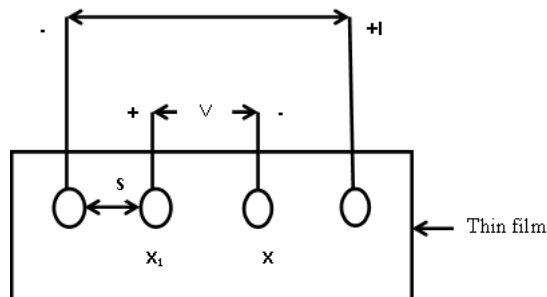


Figure 2.3: The four point probe linear set up

Elemental composition of the films

To determine the elemental composition of the films, XRF spectroscopy was used. XRF spectroscopy is widely used for the qualitative and quantitative elemental analysis of environmental, geological, biological, industrial and other types of samples. Compared to some competitive techniques such as Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Spectroscopy (ICPS) and Neutron Activation Analysis (NAA), XRF has the advantage of generally being non destructive, multi-elemental, fast and cost effective. It also provides fairly uniform detection limit across a large portion of the periodic

table and is applicable to a wide range of concentrations, from 100% to few parts per million. A main disadvantage is that analyses are generally restricted to heavier elements than fluorine.

Results and Discussion

Introduction

This chapter presents the data obtained from all experimental procedures and the various analyses carried out on the results. The trend of various graphs is also accounted for in their respective experiments.

Optical spectra of the films

Optical transmittance spectra of tin selenide (Sn_xSe_y) thin films

A plot of transmittance against the wavelength for the raw data of various samples is shown in the Figure 3.1. Generally the samples of tin selenide had low transmittance (60%) in the visible range (380nm-780nm) except the sample with ratio of 1:1 whose transmittance was 85% near 700nm. This was due to high absorption as a result of a narrow band gap. The fundamental absorption edge was between 350 nm and 650 nm although there was a shift of the absorption edge towards the shorter wavelength. Increase in carrier concentration from tin atoms blocks the lowest states in the conduction band [6]. This is attributed to Burstein Moss effect. Burstein pointed out that an increase in Fermi level in the conduction band of degenerate semiconductor leads to widening of the energy band (blue shift) [7]. The undulating pattern in the transmittance curves are caused by interference of light in the thin film itself [8].

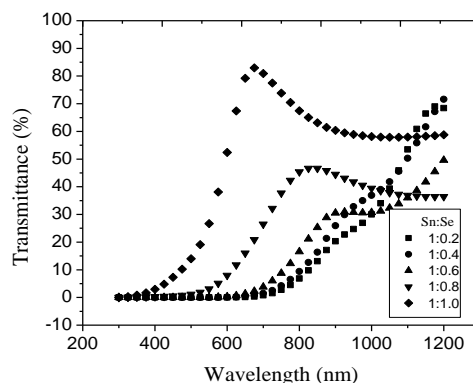


Figure 3.1: The variation of transmittance against the wavelength for various ratios of tin to selenium. The transmittance increases as the ratio approaches 1:1. Optical reflectance spectra for tin selenide (Sn_xSe_y) thin films.

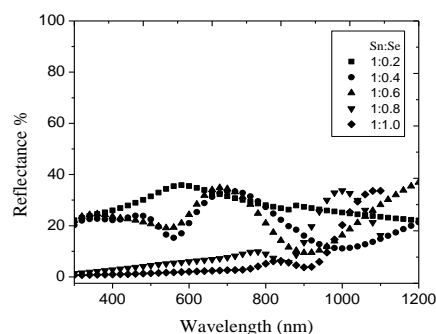


Figure 3.2: Optical reflectance spectra of tin selenide. Low reflectance indicated that the films had high absorption making the films suitable for the absorber layer.

Reflectance data Figure 3.2 shows that the average reflectance obtained within the visible range was less than 40%. Therefore tin selenide thin films exhibit high absorption behavior. This makes the material a good absorber material for solar cell applications.

Optical constants and band gap

The raw data was analyzed using the SCOUT software which uses various physical models to generate its own numerical values through simulations. The simulated data was fitted into the experimental data to obtain the optical constants such as refractive index n , absorption coefficient α , and the optical band gap E_g . The data obtained was plotted using the Microcal OriginLab™ software and the graphs such as the one in Figure 3.3 were obtained.

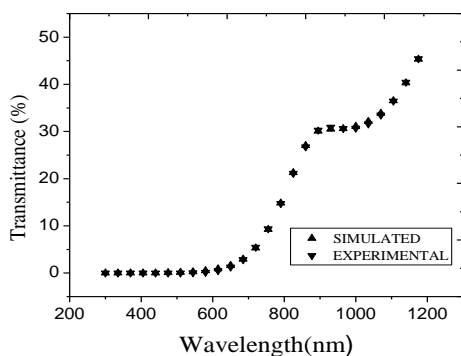


Figure 3.3: Simulated versus experimental graph for Sn:Se = 1:0.6

The optical band gap dependence of the absorption coefficient is given by the equation (3.1) where direct transitions were assumed.

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{3.1}$$

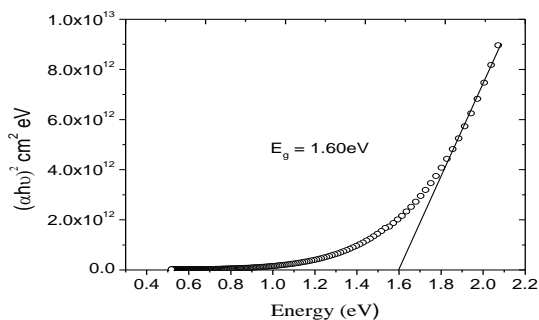


Figure 3.4: Extrapolation for the linear part for Sn:Se = 1:0.8. The band gap obtained was 1.60eV.

where A and E_g are constant and optical band gap respectively. The band gap values were obtained by plotting $(\alpha h\nu)^2$ against energy, $E (h\nu)$ (eV). The linear part of the graph was extrapolated to the point $(\alpha h\nu)^2 = 0$ on the x-axis, this gives the energy gap E_g . A sample graph is shown in Figure 3.4.

The band gap for various samples of tin selenide were obtained as in Table 3.1.

Table 3.1: The variation of tin to selenium ratios with the band gap. The band gap reduced as the ratio of tin to selenium approached 1:1.

Sample name	Sn:Se Ratio	Band gap(eV) at room temp(25°)
A	1:0.2	2.04
B	1:0.4	1.80
C	1:0.6	1.75
D	1:0.8	1.60
E	1:1.0	1.40

The values of band gap obtained were the same as those obtained directly from the SCOUT software. Although the values of band obtained were high, they were found to be within the range of those obtained by other researchers such as Kumar et al, (2012) [9] who deposited tin selenide by a similar method, (thermal evaporation), whose band gap values were 1.24eV to 1.74 eV.

Absorption coefficient for tin selenide

A plot of absorption coefficient against the wavelength from 300nm to 1200nm is shown in Figure 3.5. The absorption coefficient was high at lower wavelength but decreased with increase in wavelength. This shows that tin selenide has a high absorption coefficient in the visible range (380 -750 nm) which is an important property for forming a good absorber layer for solar cells. In addition the average absorption was more than $2.0 \times 10^5 \text{ cm}^{-1}$ which agrees with the values in literature of between 10^4 - 10^5 cm^{-1} [10]

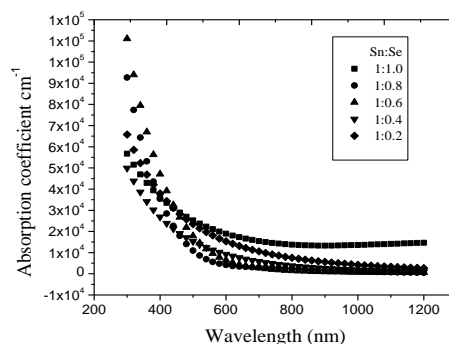


Figure 3.5: The absorption coefficient against wavelength. There was a decrease in the absorption coefficient at longer wavelength.

XRF results

The elemental analysis was carried out using the PANalytical XRF spectrometer and the data obtained direct from a computer using MiniPal software.

XRF spectrum for tin selenide (SnSe)

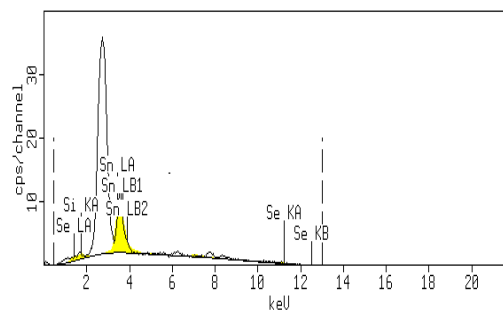


Figure 3.6: XRF spectrum for optimized SnSe (ratio 1:1)

The yellow coloured spectrum in figure 3.6 shows the composition of the elements present in the thin films at K_α , K_β , L_α and L_β lines. The elements present were Sn 51% and Se 49%. The bottom line represents the Background Radiation which shows the radiations detected by the XRF machine but are not present in the thin film samples. These radiations may have originated from the machine itself, or and the room in which the measurements were taken. The highest colourless peak represents the detector escape which is a spectrum for detector peak (Rhodium) element that the machine is made of.

Conclusion

Deposition of thin films of Sn_xSe_y was done by thermal evaporation. Although the transmittance of the films was low, it increased with increased in amount of selenium in the films

reaching a value of 85% for optimized ratio within the visible range. The band gap for the optimized films was 1.4eV while the resistivity of the films also decreased as the ratio of tin to selenium approached 1:1 reaching the lowest level of 20.1Ωcm.

Acknowledgement

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