

PREPARATION AND CHARACTERIZATION OF THIN FILM SnSe USED BY CLOSE SPACED VAPOR TRANSPORT TECHNIQUE

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In the present manuscript we have studied the preparation and characterization of SnSe thin film grown by close-spaced vapor transport (CSVT) technique. The thickness of ~10 μm film was prepared in a temperature 600°C with the deposition time 5 minutes on the SnO₂ coated soda lime glass substrate. The film was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive analysis by X-rays (EDAX), UV-vis-NIR spectrophotometer and Hall effect measurement. In this paper we present results concerning the film showed the single phase orthorhombic structure, and the orientation to the (111) plane. From SEM image the grain sizes the film was found to be 2-4 μm . SnSe film had a optical band gap of 0.92 eV with a hole concentration in the film is $4.7 \times 10^{18} \text{ cm}^{-3}$ and a p-type conduction.

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1. Introduction

In the context of photovoltaic conversion that SnS and SnSe attract the most attention of researcher. Their direct gap is close to the ideal gap of the semiconductors used in solar cell, and their absorption coefficient is high ($>10^4 \text{ cm}^{-1}$) and always p-type. As shown by a high photovoltaic conversion efficiency can be achieved with these materials. Their electrical properties are controllable.

Tin Selenide (SnSe), a member of group IV-VI semiconductors have interesting optical and electronic properties which make them potential candidates for applications in thin film solar cells. SnSe is an important binary IV-VI semiconductor compound with a wide range of potential applications with an indirect band gap of 0.9 eV and a direct band gap at 1.30 eV in the UV range (e.g., memory switching devices and infrared optoelectronic devices) [1,2]. Bulk SnSe has an orthorhombic structure close to NaCl. These structural parameters are close to those CdS, one of the optical windows in the photovoltaic and which minimizes the problems of dislocations at the level of the heterojunction solar cell. Owing to the quantum confinement effect, tunable band gaps of SnSe nanostructured materials (e.g., thin films and nanocrystals) have been demonstrated, which makes them capable of absorbing a major portion of solar energy. As an earth-abundant, environmentally benign, and chemically stable material, SnSe is placed among the most promising candidates for solar cells.

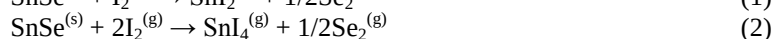
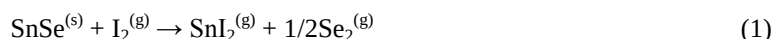
Several methods have very recently reported the thin films of SnSe using chemical bath deposition [3], atmospheric pressure chemical vapour deposition[4], electrodeposition [1,5,6], thermal evaporation [7,8], flash evaporation [9], spray pyrolysis [10,11]. In this paper we report results of preparation of SnSe thin films by a close-spaced vapor transport technique for the first time.

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2. Experimental

The CSVT system consists basically of a vertical reactor, it was made from quartz tube whose diameter can be chosen according to devices to be grown. The reactor has an inner diameter of about 2 cm and length of 10-20 cm. The source of SnSe (powder pressed at 300 kg cm^{-2} with a thickness is about 0.1 cm) and SnO_2 coated soda lime glass substrate are facing each other, and are separated by quartz spacer thickness is 0.2 cm. The transport reagent composed of solid iodine is placed in the upper part of the reactor, and then this part is sealed under vacuum pressure of 10^{-5} Torr. The complete system was installed on an external SiC rod. The source temperature depends on the electric voltage applied to this SiC heating element. The source temperature was indicated by a regulator and the temperature of the upper face of the substrate was directly measuring using a chromel-alumel thermocouples. The thermal gradient between the source and the substrate is adjusted by using a heating coil, which also allows for preheating of substrate before heating the source. Solid iodine was heated by an electrical filament to the temperature 40°C , measured by chromel-alumel thermocouples [12]. The iodine vapor decomposed the surface of the source and transported the elements SnSe to the bottom of the substrate which was colder than the source of about 50°C to 100°C . The polycrystalline SnSe ingot was synthesized in a furnace; the constituent elements are mixed in stoichiometric proportion of Sn and Se elements (99.9999% purity) and sealed in a quartz ampoule under a vacuum of about 10^{-5} Torr. The sealed ampoule is then placed in a furnace and heated to 1050°C with heating rate 10°C/h . The resulting ingot were about 3 cm long and 1 cm in diameter. The SnSe ingot was then crushed into a powder size of about $100 \mu\text{m}$ and then the powder was pressed (300 kg cm^{-2}) as a source to be used for the preparation of thin films SnSe.

In this study, the best result of SnSe film was deposited at source temperature 650°C and substrate temperature 600°C with the deposition time 5 minutes. The structural properties of as deposited film were carried out using X-ray diffraction (XRD). The composition of the film was determined by energy dispersive analysis by X-rays (EDAX) system attached to a scanning electron microscope (SEM). The optical properties of the prepared film were analyzed using double beam UV-VIS spectrophotometer. The electrical conductivity type was determined with a hot thermal probe technique. The other electrical properties of the sample were determined by Hall effect measurements at room temperature. The possible reaction growth mechanism as follows, SnSe source (Reaction 1 and 2).



Simultaneously, mixture reaction of iodides in the source of SnSe to substrate space (Reaction 3). SnSe deposition $\text{Sn}^{(l)}$ and previously released $1/2\text{Se}_2^{(g)}$ combine together between iodides and element chalcogenes to form SnSe which is deposited on SnO_2 coated soda lime glass substrate (Reaction 4 and 5).

3. Results and discussion

Fig.1 presents the XRD spectrum of a sample obtained from a source SnSe deposited on the SnO_2 coated soda lime glass substrate provided in the substrat temperatur 600°C and the temperature of the source 640°C . All these XRD spectrum indicated presence peaks at $2\theta=29.2^\circ$, 30.3° , 41.2° , 43.1° , 47.2° , 60.5° and 71.2° which can be assigned to (011), (111), (002), (202), (302), (022) and (313) planes, The peaks of the sample match those JCPDS 32-1382 and shows a very intense peak at $2\theta=30.28^\circ$ which can be attributes to orthorhombic phase. No other peaks for SnSe_2 were detected. This is the same orientation preferential peak observed by Boscher et al [4] at higher substrate temperatures of 625°C and 650°C the SnSe phase predominated.

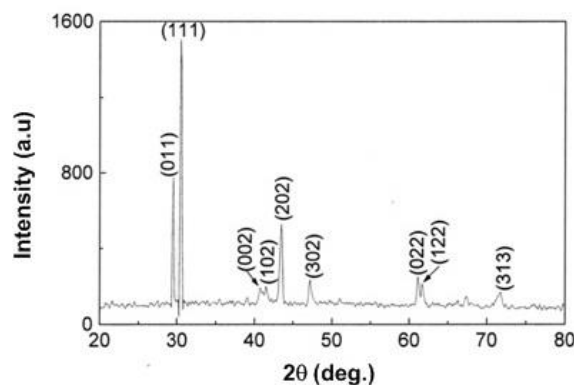


Fig.1. XRD spectrum of SnSe thin film deposited at substrate temperature 600 °C

It is observed that the progressive emergence of the diffraction peak for sample located at 30.3° a strong preferential orientation growth along the crystallographic plans (111). A similar results with preferred orientation of (111) plane was also reported by thermal evaporation technique [6,7,8]. These XRD spectra correspond to the known orthorhombic structure of SnSe with the average lattice parameters of $a = 11.39 \text{ \AA}$, $b = 4.21 \text{ \AA}$, and $c = 4.42 \text{ \AA}$, calculated from least square fitting to the Bragg peaks. Fig.2 shows the surface morphologies of $\sim 10 \text{ }\mu\text{m}$ -thick SnSe films deposited at the substrate temperature of 600°C. The SnSe film is composed of small grains with micro-bricks shape coalescing together. The average size of the bricks grains was 2-4 μm .

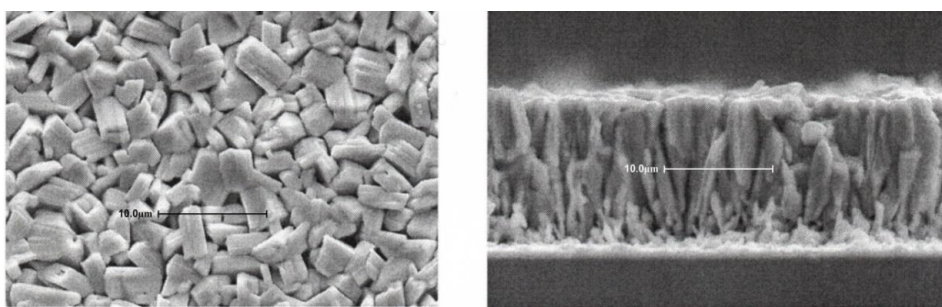


Fig.2. SEM images of the SnSe thin film prepared by CSVT and cross-sectional view image.

The surface morphology of the as deposited film shows uniform grain size without pinholes. From the cross-sectional view, sharp crystal facets can be observed on each SnSe grain which indicates improved crystallinity of the film. The film has columnar structure with grain boundaries perpendicular to the substrate. The grain size in the elongated direction is about the same size as the film thickness of $\sim 10 \mu\text{m}$. The dependence of the morphologies of SnSe on film could be changed from spherical grains to platelet-like as the deposition parameter has been previously reported by Bicer et al [4] and Boscher et al [5] and the average length of the platelets was found to be comprised between 10 μm and 40 μm .

In order to detect elemental composition of SnSe film, EDX was carried out shows that the only elements present in prepared elements are Sn and Se. No other iodide based element have been observed from EDAX result it was also found that our samples consist of Sn and Se. The overall composition of this sample (48.8 at.% of Sn and 51.2 at.% of Se). The analysis shows a decrease of selenium by large excess of tin ($\text{Sn/Se} = 0.95$). This ratio is attributed to the high vapor pressure of selenium (Se_2), which evaporates out from the reaction growth mechanism on SnO_2 coated soda lime glass substrate. Mariappan et al [11] reported a slightly selenium rich obtained from spray pyrolysis technique.

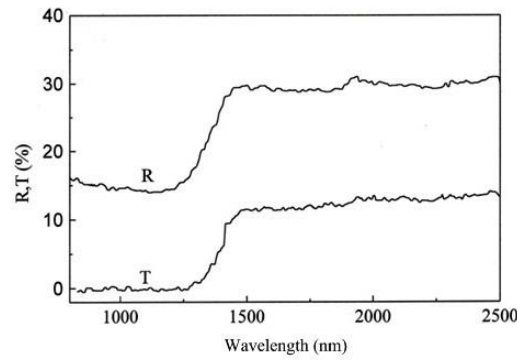


Fig.3. Reflection and transmission of SnSe thin film deposited at substrate temperature 600 °C.

The absorption coefficient (α) and the optical band gap (E_g) of the film were determined from the transmittance (T) and reflectance (R) measurements. The absorption coefficient was determined based on the following formula to minimize the interference effects in the absorption of the film [13]. Transmittance and reflectance spectra of SnSe film is shown in Fig.3. The film was transparent in the range of wavelength 800-2500 nm and their showed complete absorption at 300-1100 nm [4]. It can be seen that the transmission edge is located at around 1100 nm this value is similar to that reported by Narro-Rios et al [10]. The film showed a high absorption coefficient α about 10^{-4} cm^{-1} above the fundamental absorption edge.

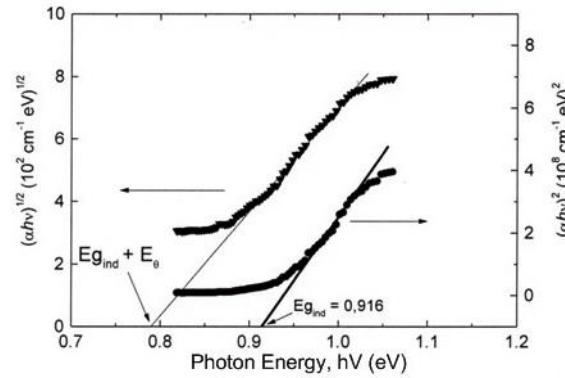


Fig. 4. Plot of photon energy ($h\nu$) as a function $(\alpha h\nu)^2$ for SnSe thin film sample

Fig.4 shows that the optical band gap of the film was determined by using Tauc relation for from extrapolation of the linear fit plot of photon energy ($h\nu$) versus $(\alpha h\nu)^2$ [14]. The straight line indicated that the gap energy for sample was found to be 0.92 eV at room temperature. The values of bands gap of SnSe film reported according to Boscher et al [4]. The optical absorption study showed the film has direct transition with band gap energy previously reported by Bicer et al [5].

The electrical properties of the films were measured at room temperature using the four probe Hall effect measurements. The SnSe thin film showed a p-type conduction. The SnSe thin films had a resistivity of $\rho = 17 \text{ } \Omega\text{-cm}$. The hole concentration in the film is $4.7 \times 10^{18} \text{ cm}^{-3}$ and the hole mobility of film was $1.56 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The carrier concentration of the film deposited is relatively high for used as an absorber material in solar cell.

4. Conclusions

Thin film of SnSe has been prepared on SnO₂ coated soda lime glass substrate by close-spaced vapor transport technique. The structural properties clearly show the strong peak orientation (111), which corresponds to SnSe films would crystallize in orthorhombic phase. The surface morphology of the films displays that the film is composed of micro-bricks like shapes. The optical band gap of the film was 0.92 eV and high carrier concentration suitable for solar cell and optoelectronic devices application.

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