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Research Article

Deposition and Structural Characterization of Sn-Se-Te Thin Films

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Abstract

In this study, the effects of Se and Te substitution on structural and morphological properties of SnSeTe (TSeTe) thin films are studied. TSeTe thin films are fabricated by using the thermal evaporation technique. In order to determine the structural and morphological properties of these films, XRD (X-ray diffraction), SEM (Scanning electron microscopy), EDXA (Energy dispersive X-Ray analysis), Raman Analysis, and AFM (Atomic Force Microscopy) measurements are carried out. Then, the effects of post-annealing on properties of thin films are investigated.

Key words: Thin Film, Structural Characterization, XRD, SEM, Raman Analysis

1. Introduction

In recent years, semiconductor thin films have drawn world-wide attention in present photovoltaic applications [1-3]. Since photovoltaic electricity is one of the best choices for sustainable energy requirements, there are studies on developing thin-film PV which reduces the cost of solar cells. Remarkable progress has been obtained in this field recently. [4-6]. The binary IV–VI compounds are getting more important in the pursuit of new semiconductor thin film materials production for solar energy. Besides their appropriate physical properties, the abundance of their component elements and their low cost are other advantages for large scale applications in this area [7].

Cadmium telluride (CdTe) is one of the most promising polycrystalline materials for thin film solar cell applications because of its physical properties [8]. High absorption coefficient (10^5 cm^{-1} at visible region) and direct band gap (about 1.5 eV at room temperature) of this material make it suitable so that thin film layers which have a few microns thickness are required for the photon absorption in which photons have higher energy than the band gap energy, and it can be obtained as p-type. In addition to laboratory studies, the efficiency of the CdTe thin films have recorded as 22.1% [9]. On the other hand, the high photosensitivity and high absorption coefficient of CdSe make it suitable for absorber layer in order to be used in photovoltaic applications [10]. However, since cadmium (Cd) is one of the heavy metals, and it is harmful to the environment, these problems cause limitations in the use of cadmium in photovoltaic industry [11].

On the researches of the IV-VI semiconductor compounds, the studies have been conducted to have eco-friendly absorber layers for photovoltaic devices by replacing Cd with Sn which is the element commonly used in the binary III-VI compounds [12]. In addition to the alternative material SnTe [13] , SnSe, p- type semiconductor material as an Se-based compound , has been investigated as another alternative absorber layer for the heterojunction solar cells due to its forbidden gap energy in the range of 0.9-1.5 eV and its high absorption coefficient [12]. $SnSe_xTe_{1-x}$ structure, which is the combination of SnSe and SnTe binary compounds that contains Se ve Te elements, is showing improvement in terms of high photosensitivity, crystalline structure, and strength [14].

In this study, the Sn-Se-Te (TSeTe) thin films have been deposited onto soda lime glass substrates where the sequential deposition of Sn, Se, and Te elements by thermal evaporation method have been used. These production parameters have been determined by analyzing systematic optimization of SnSe and SnTe thin films and their structural properties. First of all, the crystalline structure properties of TSeTe thin films and the evolution of different phases of structure will be determined by using X-ray diffraction (XRD) analysis. Then, the morphological and the chemical composition of the films will be investigated by using scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) measurements, respectively. In addition, the structural changes will be observed

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by thermal processing at different temperatures. According to the obtained results of these processes, structural modification will be studied by altering the temperature of the substrate. Finally, surface topography of the optimized TSeTe thin films will be examined by atomic force microscopy (AFM), and the elemental composition will be analyzed by EDS measurements.

2. Experimental Details

TSeTe thin films deposited onto soda lime glass substrate using sequential stacked layer growth technique by using thermal evaporation method. Firstly, the stacked layers were deposited as Sn (50 nm)/Te(50nm)/Se(50nm)/Sn(30nm)/Te(50nm). The evaporation temperatures are measured as 1400 ^{0}C, 200^{0}C and 180 ^{0}C under the vacuum ($\approx 10^{-6}$ Torr) for the powder of Sn, Te and Se, respectively. During the deposition of these layers, substrate temperature was kept constant at about room temperature and the vacuum pressure was controlled at about 10^{-6} Torr. After deposition of precursor layers, thin films annealed at 200^{0}C under vacuum during Se evaporation for half an hour. These films are labeled as asgrown sample. After deposition of SnSe$_x$Te$_{1-x}$ thin films, post-annealing processes were applied. Post-annealing processes were applied at 250 ^{0}C and 300 ^{0}C under nitrogen (N_2) atmosphere for half an hour to study the effects of post-annealing on properties of thin films. The morphological and compositional properties of the deposited films were investigated by Quanta 400 FEG model scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy analysis (EDXA) system. The X-ray diffraction (XRD) measurements were performed by using a Rigaku Miniflex XRD system equipped with a CuKα radiation source with average wavelength of 1.54 Å. Raman scattering measurements were also carried out by using Renishaw inVia confocal Raman microscope and a laser with the wavelength of 532 nm used as an excitation source. In addition, the surface morphology of the thin films was investigated in detail by using Veeco Multimode.V model atomic force microscope (AFM).

3. Results and Discussions

In this part of the analysis, ICDD (International Centre for Diffraction Data) cards were used to determine the structure, degree of crystallinity and phase compositions of the films. XRD patterns for asgrown TSeTe thin films are given in Figure 1. As can be seen from the figure, film has the polycrystalline structure. According to ICDD cards, preferred orientation is along (200) direction at 2θ= 29^0 which belongs to SnTeSe phase (Card no: 65-7394). Also, the peak from (220) plane detected at 2θ=40.9^0 belongs to SnTeSe phase (Card no: 65-7151). In addition, secondary phases are also observed such as Se along (202) (at 2θ=24.3^0, Card no: 24-0714) direction, SnTe along (200) (at 2θ=28.2^0, Card no: 65-7162) direction and SnSe along (111) (2θ=30.4^0, Card no: 89-0247) direction.

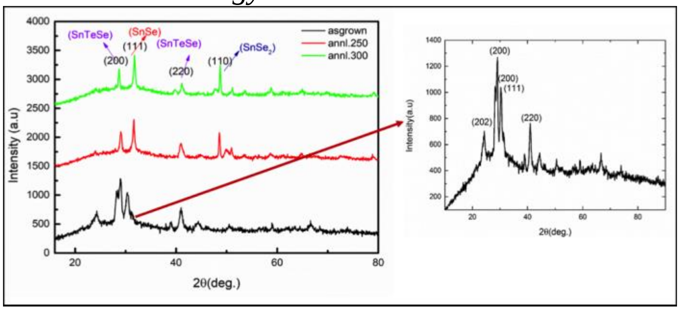

Figure 1: XRD patterns of asgrown and TSeTe thin films annealed at 250 ^{0}C and 300 ^{0}C.

when the post-annealing processes were applied, the secondary phases such as Se along (202) (at 2θ=24.3^0, Card no: 24-0714) direction that were observed in asgrown are lost at the thin films annealed at 250 ^{0}C and 300 ^{0}C. Also, the peak from (220) plane detected at 2θ=40.9^0 belongs to SnTeSe phase (Card no: 65-7151) showed a decrease in intensity with increasing annealing temperature. In addition, after the annealing temperature 250 ^{0}C, the formation of $SnSe_2$ phase occurred.

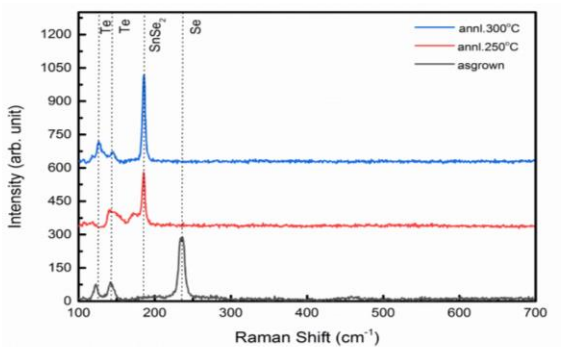

Figure 2: Raman spectra of asgrown and TSeTe thin films

annealed at 250 ^{0}C and 300 ^{0}C.

Raman analysis showed that asgrown sample has their peaks which indicate two Te peaks and one Se peak [15-16]. After the post-annealing process, the Se peak disappeared. This may be due to the re-evaporation of Se with the thermal process. Also, after the annealing, the peak belongs to $SnSe_2$ phase was observed which has an increasing intensity with increasing annealing temperature [17]. However, the peak belongs to Te phase could not be dispelled which will be seen clearly on the following section.

The surface morphology of thin films was observed by examining micrographs obtained from scanning electron microscope (SEM). The micrographs recorded for as-grown thin films, and thin films annealed at 250 ^{0}C and 300 ^{0}C are given Figure 3.

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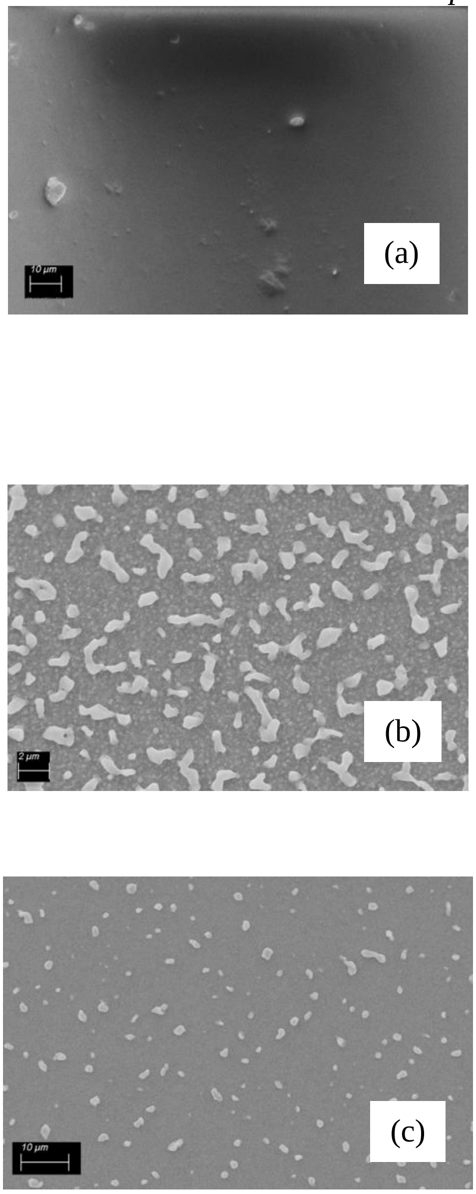
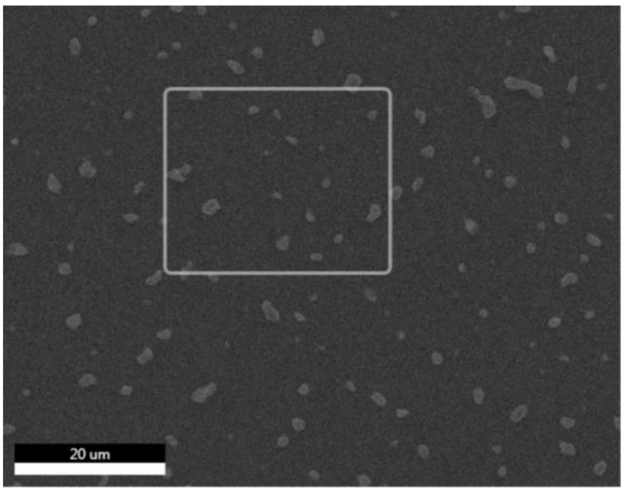


Figure 3: SEM images for for (a) agrown, (b) annealed at 250 ^{0}C (c) annealed at 300^{0}C TSeTe thin films



As can be seen from micrographs of asgrown sample, there are agglomerations over the surface. After the annealing process, it could be said that those agglomerations started to disappear slowly and get smaller as the annealing temperature increases. Since the grain sizes change, it could be deduced that post-annealing process has an effect on the morphology of the deposited thin films.

EDXA is a well-known technique to learn the chemical composition of materials. In this experiment, SEM with EDXA provided information about elemental analysis and morphology of surface. In order to investigate the effect of post- annealing on the chemical composition, EDXA measurements were carried out for as-grown thin films and thin films annealed at 250 ^{0}C and 300 ^{0}C which are listed in the Table 1.

Table 1: EDXA measurement results obtained for as-grown and annealed thin films at 250 ^{0}C and 300 ^{0}C TSeTe thin films.

	Sn(at%)	**Se(at%)**	**Te(at%)**
asgrown	9.3	54.0	36.7
annl. 250^{0}C	19.3	45.7	35.0
annl. 300^{0}C	19.2	49.5	31.3

As seen from the table, the EDXA results show that as-grown films are tin(Sn) deficient, and selenium (Se) and tellurium (Te) rich. A decrease in Te is observed with the post-annealing procedure. The fluctuations with annealing in Sn and Se could be caused by the segregation of the elements during the structure transformation from amorphous to polycrystalline.

The Figure 4 shows EDXA mapping of the thin film annealed at 300 ^{0}C. As seen from the figure that the large agglomerations seen on the SEM micrographs are caused by Te which has a high percentage. The disappearance of these agglomerations (spots) with annealing process can be the result of diffusion of Te atoms from surface to bulk.

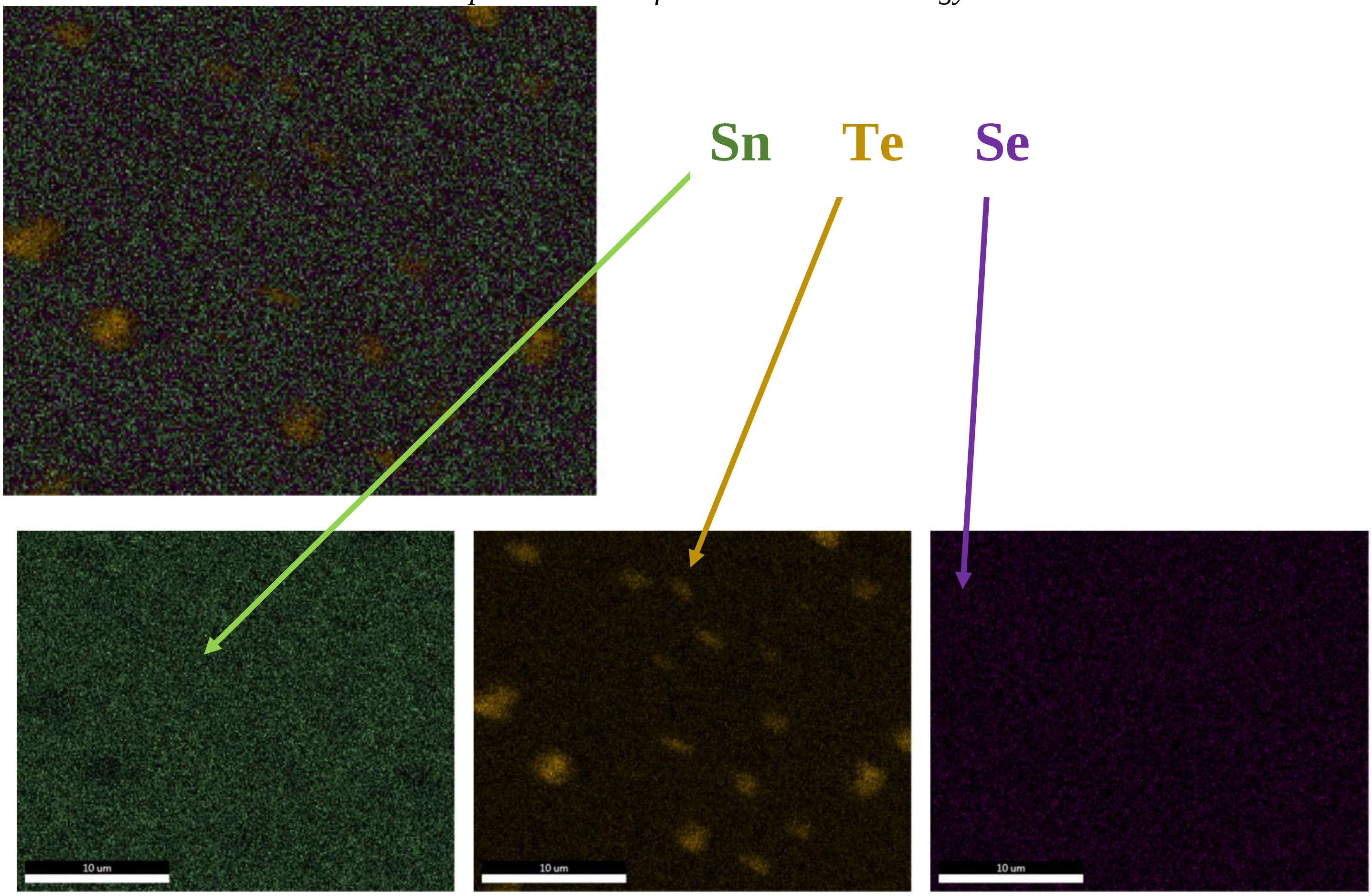
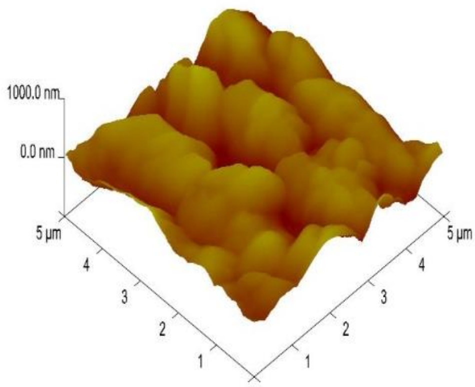


Figure 4: EDXA mapping for annealed at 300^0C TSeTe thin films

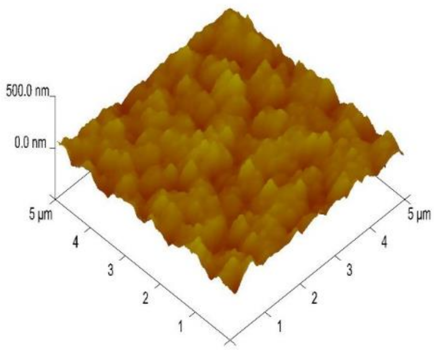
The topographic properties of the deposited TSeTe thin film samples were investigated by using AFM measurements and the observed topographic images are shown in Figure 5. As seen from the figure, there were an effect of the annealing process on both the grain size and the roughness of the films. This result is also good agreement with the SEM and EDS results. The diffusion of Te atoms from surface as mentioned above could lead to change in the topology of the films.

(b)



(c)

(a)



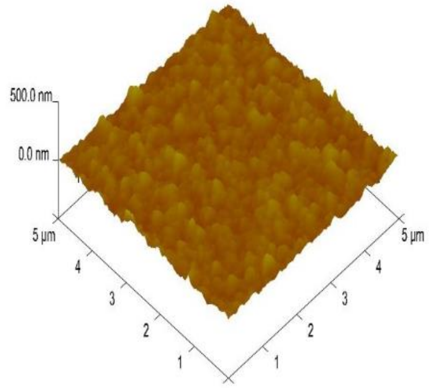


Figure 5: AFM results for as-grown and thin films annealed at 250 ^{0}C and 300 ^{0}C TSeTe thin films.

4. Conclusion

In summary, the aim of this study was to obtain pure form of SnSeTe (TSeTe)thin films and to investigate the effect of post-annealing on the structural and morphological properties of thin films. For this purpose, as-grown samples were annealed at 250°C and 300°C under N_2 atmosphere. XRD results indicates that TSeTe thin film has polycrystalline structure. X-rays scattering measurements confirm the presence of SnSeTe structure and undesired secondary phases such as Se, SnSe and SnTe. In order to get rid of the secondary phases, heat treatment or etching processes has been applied to the films. In addition, Raman scattering measurements indicate the secondary phases, which agree with EDS mapping. SEM results show the agglomeration of Te on the surface of the films and it was observed that post-annealing process has positive effect on the elimination of Te agglomeration. AFM results also indicate that post-annealing process has an effect on the topology of the films.

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