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Deposition and Characterization of $ZnSnSe_2$ Thin-Films Deposited by Using Sintered Stoichiometric Powder

Araştırma Makalesi / Research Article

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ABSTRACT

In this work, ZnSnSe2 (ZTSe) thin films were deposited using crystalline powder grown by vertical Bridgman-Stockbarger technique. The deposition process was carried out by means of e-beam evaporation on the well-cleaned soda lime glass substrates and keeping them at the substrate temperature of 200°C. The structural, optical and electrical properties of ternary ZTSe thin films were investigated depending on the annealing temperature at 250 and 300°C. X-ray diffraction analysis showed that as-grown films were in amorphous structure, however annealing at 250°C triggered the crystallization on the preferred ternary structure and annealing at 300°C resulted in the changes from amorphous to the polycrystalline structure. Using the compositional analysis, the detail information about the stoichiometry and the segregation mechanisms of the constituent elements in the structure were determined for both as-grown and annealed samples. In addition, they were morphologically characterized using scanning electron microscopy technique. The electrical properties were analyzed using temperature dependent dark- and photo-conductivity measurements. From the variation of electrical conductivity as a function of the ambient temperature, the current transport mechanisms and corresponding activation energies at specific temperature intervals for each sample were determined. The optical properties for the ZTSe thin films were studied depending on the structural changes with annealing.

Keywords: Thin film, deposition, characterization.

Sinterlenmiş Sitokiyometrik Toz Kullanırak Üretilen $Znsnse_2$ İnce Filmlerinin Üretimi Ve Karakterizasyonu

ÖZ

Bu çalışmada dikey Bridgman-Stockbarger tekniği ile büyütülen kristal toz kullanılarak $ZnSnSe_2$ (ZTSe) ince filmleri üretilmiştir. Üretim süreci çok iyi temizlenmiş sodalı kireç cam alttaşlar üzerine elektron-demeti buharlaştırması vasıtasıyla gerçekleştirilmiştir ve üretim sırasında alttaş sıcaklığı 200°C tutulmuştur. Üçlü ZTSe ince filmlerinin yapısal, optiksel ve elektriksel özellikleri 250 ve 300°C 'deki tavlama sıcaklıklarına göre araştırılmıştır. X-ışını kırınım analizi üretilmiş filmlerin amorf yapıda olduğunu gösterirken, 250°C' de istemli üçlü yapıda kristalleşmeye başladığını ve 300°C'de amorf yapıdan çoklu-kristal yapıya dönüştüğünü göstermiştir. Üretiliş ve tavlanmış filmler için kompozisyon analizi kullanılarak bileşen elementlerin yapı içindeki sitokiyometrisi ve yapıdan ayrılmaları hakkında detaylı bilgiler araştırıldı. Ayrıca, filmler elektron mikroskobu tekniği kullanılarak morfolojik açıdan karakterize edildi. Isı bağımlı karanlık ve ışık altı iletkenlik ölçümleri kullanılarak elektriksel özellikler analiz edildi. Çeşitli sıcaklıkların fonksiyonu olan elektriksel iletkenliğin değişiminden akım iletim mekanizmaları ve buna karşılık gelen belirli sıcaklık aralıklarındaki aktivasyon enerjileri her örnek için belirlendi. Tavlamayla yapısal değişimlere bağlı olarak ZTSe ince filmlerinin optik özellikleri çalışıldı.

Anahtar Kelimeler: İnce film, büyütme, karakterizasyon

1. INTRODUCTION

Silicon is the by far the most studied and commercially PV absorber when compared to other technologies. However, some drawbacks such as having the indirect band gap and the week absorption coefficient, which requires a thick absorber layer (>100µm) to absorb the all of the incident light, make Si to be far from an ideal material for PV applications. The perfect single crystal substrates are need to be used for getting high efficiency solar cell due to necessity of grain boundaries which are active recombination centers; hence raising the cost. These issues countermine to reduce the cost of Si solar cells [1]. Therefore, the developments for suitable band gap materials in the solar cell application have been crucial. Thin film solar cells are the powerful candidate to Si solar cells.

Direct band gap materials such as CdTe, $CuInS_2$ (CIS), and $CuInGa(S,Se)_2$ (CIGS) have high absorption coefficient of 10^4-10^5 cm^{-1}. Therefore, with having the thickness value of 1-2µm reduces the necessities for

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crystal quality [2]. These widely used thin film absorber layers currently demonstrate record cell efficiency of 22.9% and 22.1% for CIGS and CdTe, respectively [3], [4]. $CuInSe_2$ and $Cu(In,Ga)(Se,S$ or $Te)_2$ (CIGS) chalcopyrite thin films have been studied as suitable materials for solar cell applications due to their high absorption coefficients and direct band gap characteristics. In recent years, researches on CIGS device showed that solar cells based on this structure were about ~23% [5-9]. Therefore, this semiconductor material has become popular among other thin film materials used in the aim of manufacturing solar cells. The heterojunction of this type of solar cell structure in general consists of $CuInSe_2$ and $CuInGaSe_2$ absorber layer with CdS window layer [10]. CdS is a toxic material due to the Cd content considering large scale applications, but it is commonly used as an n-type layer. Because of the environmental risks of CdS, alternative materials such as ZnSe and ZnS have been point of interest as a window layer. However, to enhance their electrical conductivity characteristics, some dopants (i.e. Cu, Ag, Sn) are used [11-13]. On the other hand, under the concerns of price and availability, new materials have been searched instead of CIGS thin films, and due to consisting of abundant and also non-toxic elements, kesterite type, $CuZnSnTe_2$ (CZST) and $Cu_2ZnSn(Se,S)_4$ (CZTS) based thin films have become popular in solar cell applications [14]. Under the aim of both obtaining low resistive n-type window layer for possible photovoltaic applications with chalcopyrite and kesterite structures; and also being a starting ternary material for kesterite structures, ZTSe chalcopyrite semiconductor materials can be used. Intrinsically, it has a direct band gap of about 1.82 eV at room temperature and n-type conductivity behavior. In the literature, there are limited works on this thin film material deposited by thermal evaporation and chemical bath techniques [15-17].

In this work, ZTSe thin films were deposited onto soda lime glasses by thermal evaporation technique using sintered stoichiometric powder. In order to investigate the physical properties of the deposited films, structural optical and electrical characterizations were carried out.

2. MATERIAL and METHOD

In this work, ZTSe thin films were deposited onto ultrasonically cleaned soda lime glass substrates by the electron beam technique using the single crystalline source powder. For the synthesis of ZTSe single crystal, constituent elements Zn, Sn and Se in a stoichiometric ratio were placed in a quartz ampoule and then sealed following to the evacuation. After sintering process, it was put in a Crystalox MSD-4000 model three zone vertical Bridgman–Stockbarger system and the crystal growth process was carried out with a special temperature gradient as 1100, 800, and 600°C adjusted to top, middle and bottom zones of the furnace, respectively. Then, the thin film deposition was done by using the powder of this crystal as an evaporation source. These films were deposited on well cleaned commercial soda lime glass substrates in 2x2 cm^2 dimensions for structural, optical measurements, and also by using copper shadow masks in van der Pauw geometry for the electrical analysis. During the deposition under vacuum about 10^{-5} Torr, the substrate temperature was kept about 200 °C and the deposition rate was around 4-5 Å/sec which was measured by Inficon XTM/2 deposition monitor connected to the quartz thickness crystal inside the vacuum chamber. After the deposition process, the ZTSe thin films were characterized firstly in as-grown form, and then the post-growth heat treatment was applied to some of the samples to deduce the effects of annealing on the structural, optical and electrical properties of the deposited thin films. This annealing process was done using annealing furnace under the nitrogen atmosphere in the temperature range of 250-300°C for 30 minutes. Besides, the thickness of the as-grown and annealed films was measured electromechanically by a Dektak 6M profilometer. Following to the deposition and each annealing processes, the structural properties of the films were investigated by means of a Rigaku Miniflex XRD system equipped with Cu Kα radiation source of average wavelength 1.54 Å. In addition, the elemental atomic composition of the ZTSe samples was analyzed with an energy dispersive X-ray spectroscopy (EDS) facility attached to the JSM-6400 scanning electron microscope (SEM). For the electrical characterizations, under dark and illuminated conditions, the temperature dependent conductivity measurements were done between the ambient temperature of 100 and 420K on the films deposited in Van der Pauw geometry. These measurements were performed by Janis liquid nitrogen cryostat equipped with a Lake-Shore 331 temperature controller. Moreover, the samples were illuminated perpendicularly by a halogen lamp for the photoconductivity measurements under different illumination intensities varying in between 20 to 115mW/cm^2. The optical characteristics of these films were investigated from the optical transmission measurements carried out by using Perkin-Elmer LAMBDA 45 UV/Vis spectrophotometer in the 300-1000 nm wavelength region

3. RESULTS and DISCUSSION

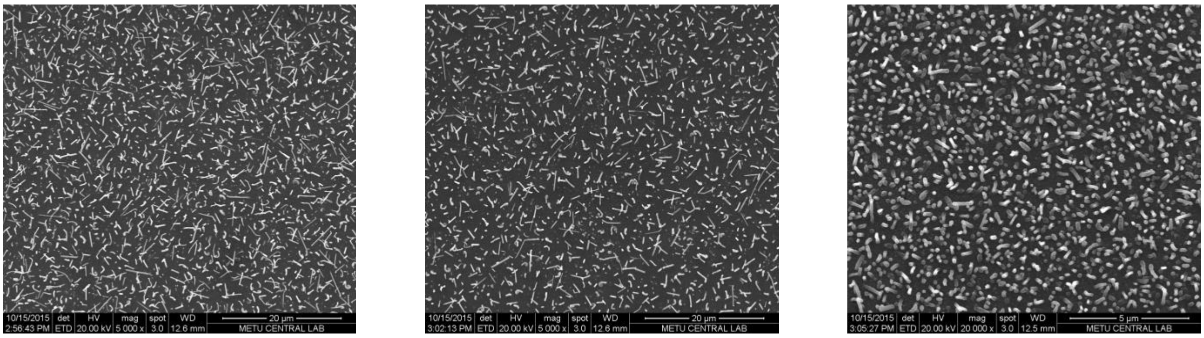
The thicknesses of the films were measured electromechanically by a profilometer and the measured film thicknesses were 420, 410 and 380 nm, for the as-grown films, and films annealed at 250 and 300°C, respectively. According to these results, the slight decrease in the thickness values could be taken as the indication of the decrease in the amount of some constituent elements in the structure of the films. In order to determine atomic ratio of the constituent elements in the deposited thin films before and after the annealing processes, EDS measurements were studied and the corresponding results were listed in Table-1. By considering the given data, the as-grown films were in Sn deficient and Zn rich behavior. In addition, these compositional characteristics were preserved with all annealing process whereas Se ratio in the composition was decreased at the 300°C annealing.

Table 1. EDS results of as-grown and annealed ZTS thin films

Sample	Zn (%)	Sn (%)	Se (%)
As-grown	37.7	18.5	43.8
Anl-250	35.6	20.6	43.8
Anl-300	43.7	16.1	40.2

The surface morphology of the films was shown in Figure 1. As seen in this figure, in addition to the few variations on the surface characteristics with annealing, there was nanowire like formations on all of the films in both as-grown and annealed forms. These formations were distributed irregularly over the film surface and they were defined as Zn crystallites according to the detailed compositional analysis. Considering the change in the thickness with the annealing, SEM images showed that annealing at 250°C significantly affected the surface morphology of the films. On the other hand, the shape of nanowire like formations started to be changed with the annealing at the 300°C. Therefore, these features found on the film surfaces can be the indication of Zn-rich materials.

In order to investigate the crystal structure of the ZST thin films, XRD measurements were done on as-grown and all the annealed samples.



(a) (b) (c)

Figure 1. SEM micrographs of the ZTS thin films (a) in as-grown form and annealed at (b) 250°C and (c) 300°C.

XRD patterns for as-grown and annealed samples at 250-300°C were shown in Figure 2. As shown in this figure, ZTSe thin films in as-gown form without any annealing process were in amorphous; but the annealing provides necessary thermal energy to construct the polycrystalline structure. According to the International Centre for Diffraction Data (ICDD), the main orientation peak of the deposited ZTSe films was found at 2θ~27° along (112) direction [10]. The peak intensity of this preferential orientation reflection of the ZTSe phase was seen in all XRD spectra. In addition, the binary ZnSe phase in (220) orientation direction at 2θ~43° [18] was observed for annealing at 250°C, after carrying out detailed analysis for this phase. By increasing annealing temperature, the peak of the preferential orientation (112) became more intense and the secondary phase was disappeared. The disappearance of the ZnSe secondary phase could be explained with the inclusion ZnSe into ZTSe lattice [19]. However, there was no noticeably change in peak positions of samples annealed at different temperatures.

Temperature dependent conductivity values for ZTSe thin film deposited in Van der Pauw geometry and annealed at 300°C were given in Figure 3. Room Temperature resistivity value was obtained about $2x10^5$ Ω for as-grown samples and this values scaled up to about $5x10^6$ **Ω** with annealing procedure. Moreover, temperature dependent conductivity measurements revealed Arrhenius behavior for all samples. While ZTSe samples were displaying a sharp change at the high temperature region, they pointed out a weak response to temperature dependence at the low temperature region.

ZTSe thin film samples showed thermionic emission characteristics as a conductivity behavior in the high temperature region of 250-420K.

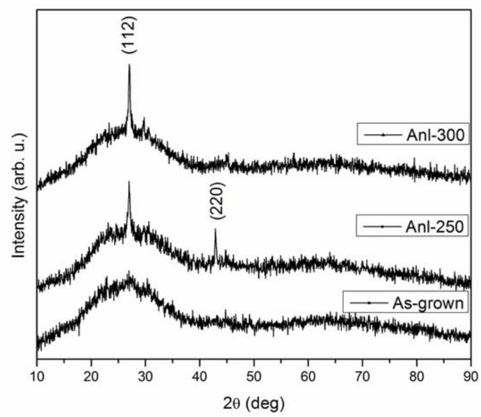


Figure 2. XRD patterns of the ZTS thin films without annealign process and with annealing at 250 and 300°C

In this temperature range, charge carriers are able to have energy to exceed conduction band and join conduction with the effect of temperature. Thermionic emission can be analyzed by the equation [20],

$$\sigma_T = \sigma_{0T}\, exp\left[-\left(\frac{E_a}{kT}\right)\right] \quad (3)$$

The thermal activation energy for ZTSe samples was calculated from the slope of ln(σ(T))-1/T plot. These values were about 116, 57 and 66 meV for as-grown and the annealed at 250 and 300°C ZTSe thin films respectively. In addition, at the low temperature region in between 100 and 250K, the conduction mechanism of these films was also analyzed with thermionic emission model and the activation energies obtained as 28, 25 and 45 meV. According to photoconductivity measurements, it was observed that increasing illumination intensity resulted in the increasing conductivities of the as-grown, and annealed at 250 and 300°C ZTSe thin films.

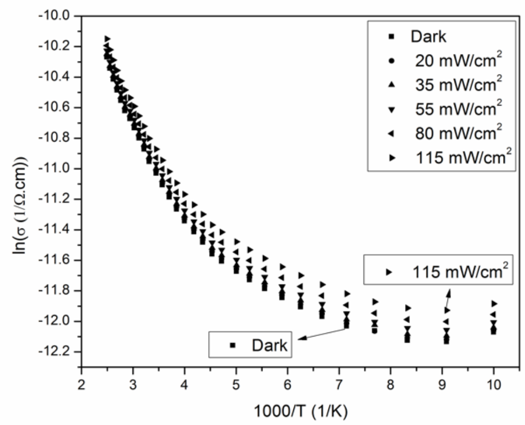


Figure 3. Temperature dependent conductivity values for the annealed at ZTSe sample 300°C

In order to determine the optical properties of ZTSe thin films, the transmission measurements were carried out in between 300-1000 nm and given in Figure 4 for as-grown and annealed films.

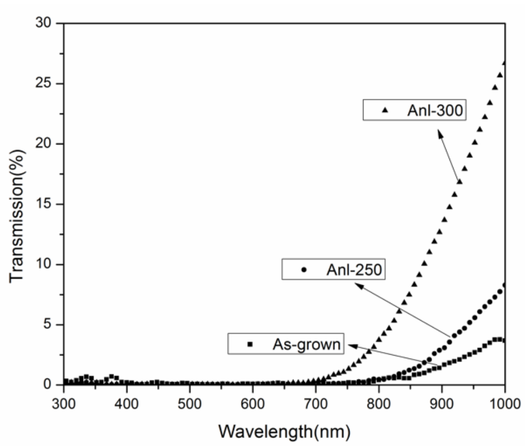


Figure 4. Transmission measurements for as grown and annealed ZTSe samples at 250°C'and 300°C

According to the measurements, transmission of the films increased with the annealing temperature. Absorption coefficient (α) obtained from the transmission measurements were in between $5x10^4$ and $8x10^4$ cm^{-1}. Then, the band gap values were calculated by extrapolation of $(\alpha h\nu)^2$ vs. hν plot as about 1.8 eV and 1.6 eV for as-grown and annealed at 300°C ZTSe thin films respectively.

6. CONCLUSION

In this work, the material characterization of the e-beam evaporated ZTSe thin films were investigated for the as-deposited and annealed samples at different temperatures. According to the structural analysis, deposited thin films were found to be Sn-deficient, and with the annealing Se concentration decreased due to possible re-evaporation from the surface. Nanowire-like shapes were seen on the film surfaces and it is deduced that these shapes were changed with the annealing at 300 ^{0}C. Moreover, deposited ZTSe films were in amorphous nature. With the annealing process they showed (112) orientation with annealing processes and secondary phases of ZnSe were disappeared with the annealing at 300 ^{0}C. On the surface of the films, Zn crystallites were observed and they were showed Zn-rich characteristic. From the electrical analysis, the Arrhenius behavior was obtained in the conductivity values above the room temperature. Thus, using thermionic emission model, activation energy values were calculated about 116, 57 and 66 meV for these films in as-grown and annealed forms respectively. The room temperature optical transmission measurements were performed on the samples before and after the thermal treatment, and from the absorption coefficient - photon energy variations of the ZTSe films, the fundamental band gap values were calculated as 1.8 eV and 1.6 eV for as-grown and annealed at 300°C ZTSe thin films respectively.

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