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Influence of pre-annealing Cu-Sn on the structural properties of CZTSe thin films grown by a two-stage process

M.A. Olgar[a,b,*], B.M. Başol[c], M. Tomakin[d], A. Seyhan[a,b], E. Bacaksız[e]

[a] Department of Physics, Nigde Omer Halisdemir University, Merkez, 51240 Nigde, Turkey
[b] Nanotechnology Application and Research Center, Nigde Omer Halisdemir University, Nigde, Turkey
[c] Active Layer Parametrics,, 5500 Butler Lane, Scotts Valley, CA 95066, USA
[d] Department of Physics, Recep Tayyip Erdogan University, Rize, Turkey
[e] Department of Physics, Karadeniz Technical University, Merkez, 61080 Trabzon, Turkey

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ABSTRACT

In this study CZTSe thin film were synthesized by a two-stage process that included sequential sputter deposition of Cu and Sn layers forming a Cu/Sn structure, pre-annealing the Cu/Sn structure at 200–380 °C for some of the samples, sputtering of additional Zn and Cu over the Cu/Sn structure, evaporation of a Se cap forming a Cu/Sn/Zn/Cu/Se precursor film, and exposing the precursor film to high temperature annealing treatment at 550 °C for 15 min to form the compound. The results of the characterization carried out on the compound layers revealed that the phase content, composition and microstructure of these layers changed noticeably depending on whether or not a pre-annealing step was utilized. Although XRD studies suggested presence of secondary phases, especially in the non-pre-annealed samples, the data was dominated by kesterite CZTSe phase reflections. Raman spectra of the films verified the formation of kesterite CZTSe structure and some other phases, which were determined to be $SnSe_2$ and possibly ZnSe. SEM micrographs showed denser structure in the pre-annealed samples.

1. Introduction

Si-based solar cells constitute a major part of PV industry (> 80%) [1]. However, this technology depends on indirect band gap material [2]. Hence, a thick layer of the semiconductor material is required to absorb the incident photons. To decrease the cost of manufacturing, PV industry have concentrated on thin film PV technologies employing much thinner semiconductor films. Thin film technologies employ direct band gap materials with high optical absorption coefficients, such as $Cu(In,Ga)Se_2$ (CIGS) and CdTe. Although CIGS and CdTe based thin film solar cell efficiencies are above 20% [3,4], toxicity of Cd and scarcity of In, Ga, and Te limit the manufacturing volume of these technologies [5,6].

$Cu_2ZnSnS(e)_4$ (CZTS(e)) have been demonstrated as an alternative PV material composed of earth-abundant elements. Kesterite is the most stable crystal structure of CZTS(e) compound, which has reported optical direct band gap values in the range of 0.9–1.6 eV and high absorption coefficients ($\geq 10^4\ cm^{-1}$) in the visible spectrum range [7,8]. CZTS(e) thin films have been grown mostly by two-stage processes. In the first stage of a two-stage process, a precursor layer is prepared employing many different techniques. The second stage involves a high temperature anneal, which causes reaction between the constitute elements within the precursor layer and/or the annealing atmosphere and forms the compound. The most commonly used vacuum-based methods for the preparation of the precursor layer include thermal evaporation [9], RF and DC magnetron sputtering [10,11] and e-beam evaporation [12]. The non-vacuum techniques include electrodeposition [13], spray pyrolysis [14], sol-gel deposition and spin-coating [15]. In the second stage of the two-stage process, high temperature annealing and reaction may be performed by conventional thermal processing or by rapid thermal processing (RTP). In some approaches elemental sulfur/selenium powders or $H_2S(e)$ gas may be used as a source of sulfur/selenium atmosphere during annealing which is generally carried out at temperatures above 450 °C. Although, the theoretical Shockley-Queisser limit for conversion efficiency of CZTS(e) based thin film solar cell is about of 32.4% [16], the highest reported conversion efficiency value to date is 12.6% [17], which is still far away from the theoretical limit. The large gap between the theoretical limit and the reported efficiency may be attributed to many reasons. For example, relatively low growth temperatures (450–500 °C) seem to be

* Corresponding author at: Department of Physics, Nigde Omer Halisdemir University, Merkez, 51240 Nigde, Turkey.
E-mail address: mehmetaliolgar@ohu.edu.tr (M.A. Olgar).

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better for CZTS(e) thin film fabrication with respect to compositional control since such temperatures avoid the loss of relatively volatile elements and compounds such as Zn and Sn-Se out of the formed compound layer. However, low temperatures may deteriorate grain growth and they may cause secondary phase formation due to inadequate reaction between constituent elements. In a two-stage process employed in CZTS(e) growth the precursor layers often contain metallic stacks comprising Cu, Sn and Zn elemental layers. The order of these elements in the stack and any pre-annealing process applied to the stack before the reaction step may also influence the properties of the compound layer obtained. Therefore, selection of proper precursor preparation processes as well as proper growth parameters applied during reaction [18] play a significant role in the fabrication of high quality CZTS(e) thin films.

In this study, a high reaction temperature (550 °C) was chosen for the second stage of the process in order to attain the desired large-grain microstructure. In order to limit the loss of Sn-Se compound at this high temperature, on the other hand, a pre-annealing step was carried out after the deposition of Cu and Sn layers on the Mo coated glass substrate. The idea was to form a relatively stable Cu-Sn alloy, and therefore reduce the chance of Sn loss from the film during compound formation. The Mo/Cu/Sn/Zn/Cu metallic stack was used in this study since promising results were previously obtained using this structure [19]. Influence of the above mentioned pre-annealing process on the properties of the CZTSe thin films was explored.

2. Experimental

Three types of metallic stacks were fabricated in this work. The first type of stack was obtained by sequential deposition of Mo/Cu/Sn/Zn/Cu using DC magnetron sputtering from high purity Cu (5 N), Sn (4 N) and Zn (4 N) targets. The base pressure of the sputtering chamber was around of 10^{-6} mbar and the operating pressure was about of 10^{-3} mbar. The thicknesses of the films deposited were about 175, 230, and 165 nm for Cu, Sn, and Zn layers respectively. Sputtering rate of each element was pre-determined through many calibration runs and the final thickness of the films were measured by Bruker DektakXT surface profilometer. A major part of the Cu (70%) thickness was deposited on top of the Mo layer and the remaining part (30%) on top of the Zn layer. The second type of stack preparation involved a pre-annealing treatment of the Mo/Cu/Sn structure in a tube furnace in a static 5%H_2 + 95%Ar atmosphere at a temperature of 200 °C for 3 min. Then, the Zn and Cu layers were deposited on the pre-annealed structure forming the final stack. The third type of stack was produced by pre-annealing the Mo/Cu/Sn structure in a tube furnace in a static 5%H_2 + 95%Ar atmosphere at a temperature of 380 °C for 6 min. After the pre-annealing treatment, the remaining Zn and Cu layers were deposited on that structure. The CZTSe layers prepared using the three types of metallic stacks were denoted as CZTSe-AD, CZTSe-200, and CZTSe-380 for the first, second, and third type of stacks, respectively. The “AD” abbreviation refers to “as-deposited” since no pre-annealing process was used in this metallic stack. The numerical values (200 and 380) refer to the pre-annealing temperature. Table 1 shows the description of these samples.

After preparation of the metallic stacks described in Table 1, Se cap layers were evaporated on top of these structures, forming precursor layers. The Se cap layers were obtained by thermal evaporation of Se (5 N) shots at a pressure of 10^{-5} mbar. The thickness of the Se caps was about 1300 nm, which was 1.4 times the amount needed to form single phase CZTSe layers based on the calculations made using the thicknesses of the Cu, Zn and Sn layers in the metallic stack. More experimental details about the thermal evaporation process can be found in one of our previous publications [20].

After evaporation of the Se cap on the metallic stacked films, the Mo/Cu/Sn/Zn/Cu/Se precursor layers were annealed for 15 min in a tube furnace in a static 5% H_2 + 95%Ar atmosphere at 550 °C. The estimated ramp rate of the temperature was about of 1 °C/s. Some Sn(II) Se powder with 4 N purity was placed at the area around the samples to create an overpressure of Sn and Se in the tube in order to prevent excessive loss of Sn-Se. The crystalline structure of the CZTSe thin films was characterized by XRD measurements using Rigaku SmartLab

Table 1
Processing information for the preparation of metallic stacked layers used in CZTSe film growth.

Sample	Pre-annealing of Mo/Cu/Sn	Pre-annealing temperature	Complete stacked films
CZTSe-AD	–	–	Mo/Cu/Sn/Zn/Cu
CZTSe-200	3 min	200 °C	Mo/Cu/Sn/Zn/Cu
CZTSe-380	6 min	380 °C	Mo/Cu/Sn/Zn/Cu

Table 2
Atomic ratios of Cu/Zn/Sn/Cu metallic stack and CZTSe thin films obtained from EDX measurements.

Sample	Cu/(Zn + Sn)	Cu/Sn	Zn/Sn	Se/Metal
Cu/Sn/Zn/Cu	0.77	1.75	1.25	–
CZTSe-AD	0.94	1.88	1.00	1.03
CZTSe-200	0.74	1.88	1.55	1.03
CZTSe-380	0.85	1.81	1.11	1.00

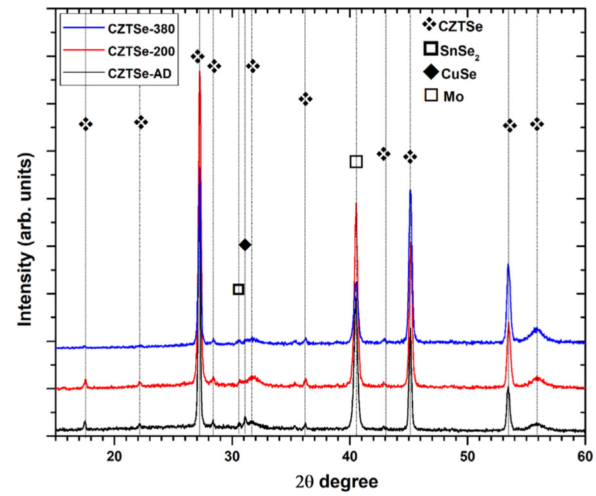

Fig. 1. XRD diffraction pattern of CZTSe thin films.

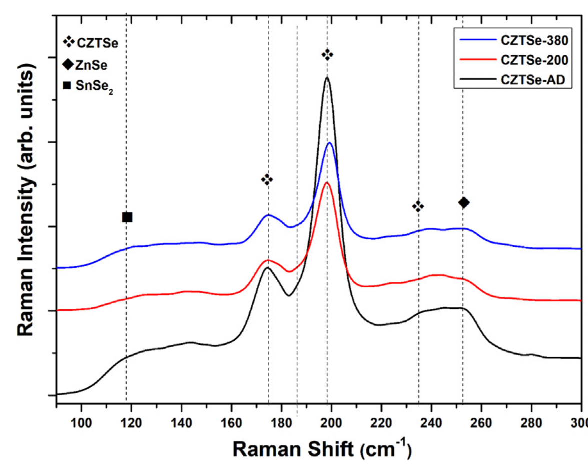

Fig. 2. Raman spectra of CZTSe samples.