GROWTH AND CHARACTERIZATION OF $(ZnSe)_{0.1}(SnSe)_{0.9}$ FILMS FOR USE IN THIN FILM SOLAR CELLS

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ABSTRACT: $(ZnSe)_x(SnSe)_{1-x}$ films were fabricated from ZnSe and SnSe precursors using chemical-molecular beam deposition (CMBD) method at a substrate temperature of 500°C. The structural and morphological properties of $(ZnSe)_{0.1}(SnSe)_{0.9}$ films have been studied. The data from the scanning electron microscope showed that the grain sizes of the films were 5-6 μm and the films had a close-packed polycrystalline structure. The results of X-ray diffraction analysis of the samples revealed that the films have an orthorhombic structure. Structural parameters of the obtained films are given.

Keywords: $(ZnSe)_x(SnSe)_{1-x}$, CMBD based deposition, thin film, absorber layer

INTRODUCTION

At present, CdTe and $Cu(In,Ga)Se_2$ based absorber layers are one of the most suitable materials for thin-film solar cells due to their basic properties. These elements have an optimal bandgap at room temperature E_g = 1.5 eV for CdTe and 0.9-1.7 eV for $Cu(In,Ga)Se_2$, which cover the entire spectrum of the infrared and visible region of the solar radiation and have high absorption coefficient (~ 10^4 -10^5 cm^{-1}), allowing the effective absorption for incident solar radiation by a thickness of several microns. This significantly reduces the material consumption compared to silicon based solar cells.

The recent advances of the thin-film solar cells, i.e. obtained by various methods and scientific centers, are presented in Table 1. As shown, the efficiency of the thin film solar cells increases regularly. The leading companies in this field are First Solar and ZSW, where the highest efficiency values have been reported for CdTe and $Cu(In,Ga)Se_2$ based solar cells, being 22.1% [1] and 22.3% [2] in laboratory conditions and 16.1% [3] and 17% [4]in the modules, respectively.

Despite the high efficiency of solar cells based on these materials, their further application on a large scale is limited due to the limited In, Ga, Te in the earth's crust, as well as the high price of Ga.

Therefore, many research centers and laboratories conduct research to replace the abovementioned expensive materials with Earth abundant elements based compounds such as Cu_2ZnSnS_4 (CZTS). This absorber layer is not only cost effective and non-toxic, but also has similar optical properties to that of $Cu(In,Ga)Se_2$ absorber layer.

As depicted in Table 1, $Cu_2ZnSnS_xSe_{4-x}$ based solar cells has achieved the efficiency of 12.6% [5] reported by the IBM research center. However, this efficiency is still lower than that of $Cu(In,Ga)Se_2$. According to Ref. [6], low efficiency of CZTS is due to the complexity of sample preparation methods and controlling the film composition.

To date, novel absorber layers such as SnSe, SbSe, $Cu_2(Sn_{1-x}Ga_x)Se_3$ (CTGS), and Cu_2SnS_3 have been studied and developed, which are made up low cost and non-toxic elements. These materials are attractive due to their similar optical properties to $Cu(In,Ga)Se_2$, e.g. their bandgap lies in the range 0.87-1.7 eV [7.8]. The initial attempts to obtain thin film solar cells on their basis yielded an efficiency of 4-6% [8]. Currently, researchers are working to further increase the efficiency of such solar cells.

Despite the fact that in the world literature there is no information on zinc and tin selenide ($(ZnSe)_x(SnSe)_{1-x}$) thin films, we believe that this material is ideally suited for use in photovoltaics. It is consisted of Earth abundant and environmentally friendly elements and has the following excellent properties:

- The bandgap can vary over a wide range of (0.9 ÷ 2.7) eV, which is suitable for the absorber layer with an optimal bandgap of 1.45 eV.
- The absorption coefficient is in the range of (10^4 ÷ 10^5) cm^{-1}. This means that an absorber layer with a thickness of (0.5÷1.0) μm is sufficient for manufacturing highly efficient solar cells.

In previous study, we investigated the physical properties of SnSe thin films [11]. In this study, we report on structural and morphological properties of $(ZnSe)_x(SnSe)_{1-x}$ thin films with x=0.1.

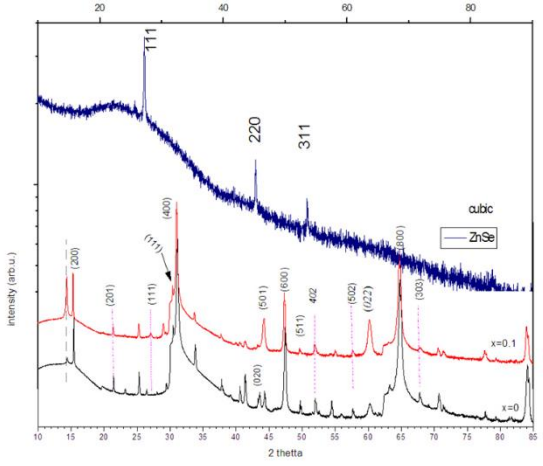


Figure 1. X-ray data of ZnSe and $(ZnSe)_x(SnSe)_{1-x}$ films for indicated x values, which were grown at a substrate temperature of 500 °C.

Table 1. Recent advances on CdS/CdTe, $Cu(In,Ga)Se_2$ and $Cu_2ZnSnS_xSe_{4-x}$ based thin film solar cells' efficiency obtained by various methods and companies [9,10]

Year	Structure	CdS and CdTe/ process	Activation process	V_{OC} (mV)	I_{SC} (mA/cm^2)	FF (%)	η (%)	Size (cm^2)	Research group
1993	glass/SnO_2:F/CdS/ CdTe	CBD/ CSS	$CdCl_2$ heat treatment	843	25.1	74.5	15.8	1.05	USF
2001	glass/CTO/ ZnO/CdS/CdTe	CBD/ CSS	$CdCl_2$ heat treatment	845	25.9	75.5	16.5	1.03	NREL
2013	glass/CTO/ ZnO/CdS/CdTe	CBD/ CSS	$CdCl_2$ heat treatment	875	28.9	78.0	19.7	1	First Solar
2014	glass/CTO/ ZnO/CdS/CdTe	CBD/ CSS	$CdCl_2$ heat treatment	872	29.5	79.5	20.4	1	First Solar
2014	glass/CTO/ ZnO/CdS/CdTe	CBD/ CSS	$CdCl_2$ heat treatment	903	30	79.8	22.1	1	First Solar
2013	glass/Mo/CIGSe /CdS/ ZnO/ZnO:Al			757	34.8	79.1	20.8	0,5	ZSW
2014	glass/Mo/CIGSe /CdS/ ZnO/ZnO:Al			746	36.6	79.3	22.3	0.5	ZSW
2008	glass/Mo/CZTS /CdS/ ZnO/ITO	Thermal evaporation		661	19.5	65.8	8.4	0.46	IBM
2012	glass/Mo/CZTSS /CdS/ZnO/ITO	Growth in solution		460	34.5	69.8	11.1	0.44	IBM
2013	glass/Mo/ CZTSS /CdS/ZnO/ITO	Growth in solution		513 .4	35.2	69.8	12.6	0.44	IBM

PM - printing method; CSS – closed-space sublimation; CBD - chemical bath deposition; USF - University of South Florida; NREL - National Renewable Energy Laboratory; ZSW – Zentrum für Sonnenenergie und Wasserstoff-Forschung (Center for Solar and Hydrogen Energy Research); IBM - International Business Machines. CTO – Cd_2SnO_4; CIGS – $Cu(In,Ga)Se_2$: CZTS – Cu_2ZnSnS_4; CZTSS – $Cu_2ZnSnS_{4-x}Se_x$

EXPERIMENTAL

The preparation of polycrystalline $(ZnSe)_x(SnSe)_{1-x}$ thin films was carried out according to the procedure described in [12]. The temperature of precursor is in the range (850-950) ^oC, whereas the substrate temperature is varied in the range of (500-600) ^oC. The carrier gas, i.e. hydrogen, flow was ~ 20 cm^3/min. The deposition time depends on the required thickness of the films and ranges from (30-60) minutes. Borosilicate glasses were used as substrates.

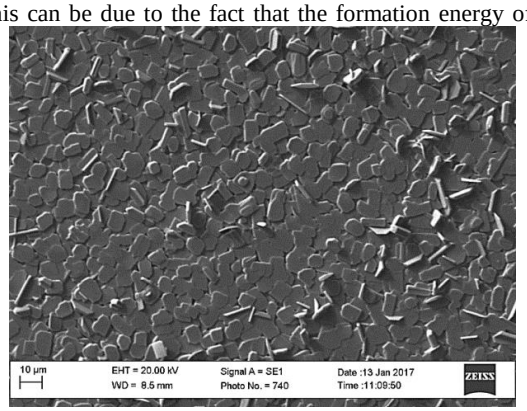
The crystal structure and the phase composition of the materials were studied by X-ray diffraction ("Panalytical Empyrean" diffractometer with CuKα radiation ,λ = 1. 5418 ˚A) with 2θ in the range of (20-80) ° and a step of 0. 010. Analysis of the phase composition was performed using the Joint Committee on Powder Diffraction Standard (JCPDS) database. Morphological studies were carried out with the scanning electron microscope (SEM-EVO MA 10). The resulting $(ZnSe)_{0.1}(SnSe)_{0.9}$ thin films had a smooth surface without cracks and pores.

RESULTS AND DISCUSSIONS

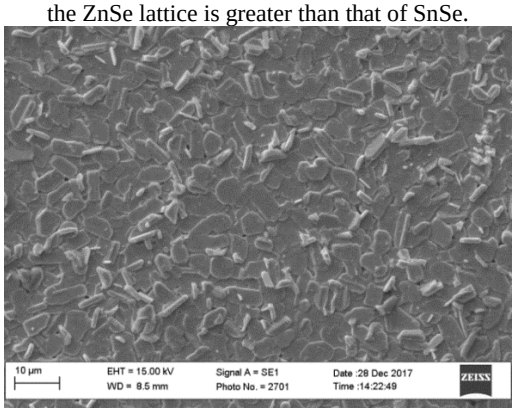
Figure 1 shows the XRD pattern for $(ZnSe)_{0.1}(SnSe)_{0.9}$ thin films obtained at a substrate temperature of 500 °C. As shown, the main peaks are corresponding to those of (400) and (800) planes. The total intensity of the (400) and (800) peaks was about 90-95% of the total intensity of all the film peaks $(ZnSe)_{0.1}(SnSe)_{0.9}$. In addition to these peaks, other peaks corresponding to the (200), (201), (111), (400), 600), (511), (402), (502), (303) and (323) planes are observed, although their intensity was extremely small compared to those of former peaks. These peaks also correspond to the SnSe peaks which is present in the phase (see Figure 1). According to XRD data, all films have an orthorhombic structure. The crystal lattice parameters for the samples were calculated by the following formula: $1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$, where d is the distance between the planes, h, k, l - Miller indices. The parameters of the lattice constant for films deposited from ZnSe and SnSe compounds at the substrate temperature of 500 ^oC have the following values: a = 11.48 Å, b = 3.78 Å, c = 4.47 Å. The structural parameters of all films are presented in Table 2. As shown, the values of a and b lattice parameters for $(ZnSe)_{0.1}(SnSe)_{0.9}$ films decrease, whereas the value of c increases. This phenomenon is explained by the fact that when the molar content of ZnSe in the vapor phase increases during the $(ZnSe)_x(SnSe)_{1-x}$ film deposition, tin atoms are replaced by zinc atoms. It is known that the ionic radius of zinc (Zn + 0.88 Å) is much smaller than the ionic radius of tin (Sn + 2 0.93 Å).

Figure 2 shows SEM images for $(ZnSe)_x(SnSe)_{1-x}$ samples deposited at a substrate temperature of 500 °C. As shown, the grain shapes of the samples had a flattened appearance with the grain sizes of about 5-6 μm. The shape and grain size of the samples changes depending on the film composition. Increased molar content of ZnSe in $(ZnSe)_x(SnSe)_{1-x}$ films led to a decrease in the grain size, and the shape of the grains retained their previous form corresponding to the composition film with x = 0.

This can be due to the fact that the formation energy of the ZnSe lattice is greater than that of SnSe.



x=0



x=0.1

Figure 2. SEM images of $(ZnSe)_x(SnSe)_{1-x}$ films for indicated *x* values.

Table 2. Structural parameters of $(ZnSe)_x(SnSe)_{1-x}$ films with *x*=0.1 grown at substrate temperature of 500°C.

2Θ	(h k l)	d (Å)
15.4	(2 0 0)	5.75
25.3	(201)	3.51
27.14	(1 1 1)	3.28
31.06	(4 0 0)	2.87
47.4	(6 0 0)	1.9
49.6	(5 1 1)	1.8
51.9	(4 0 2)	1.75
57.7	(5 0 2)	1.59
60.26	(2 0 2)	1.5
64.86	(8 0 0)	1.4
67.9	(3 0 3)	1.3
84.02	(3 2 3)	1.15

SUMMARY

The results of the XRD and SEM data revealed that: 1) the films have an orthorhombic polycrystalline structure; 2) the grain sizes of the films are 5-6 µm and the films have a close-packed polycrystalline structure, and 3) increased molar content of ZnSe in $(ZnSe)_x(SnSe)_{1-x}$ films led to a decrease in the grain size, and the shape of the grains retained their previous form.

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