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Growth and characterization of $Zn_xSn_{1-x}Se$ films for use in thin film solar cells

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Abstract

We have fabricated $Zn_xSn_{1-x}Se$ (ZTS) films for the first time. Samples were fabricated by chemical molecular beam deposition method at atmospheric pressure in hydrogen flow. ZnSe and SnSe powders with 99.999 % purity were used as precursors. The temperature of precursors varied in the range of (850 – 950) °C. Films were deposited at substrate temperature of (500 – 600) °C. Borosilicate glass was used as a substrate. We have studied ZTS films by EDS, XRD and SEM. The samples had orthorhombic and cubic structures depending on substrate temperature. Results of EDS have shown that composition of samples moved to ZnSe side with substrate temperature. SEM pictures have shown that samples had polycrystalline structure. The grain size varied in the range of (2-15) µm. The grain size of samples increased from (2-5) µm to (15 -20) µm for substrate temperatures of 500 °C and 550 °C respectively. While, at substrate temperature of 600 °C the grain size decreased up to (3-5) µm, possibly, because of increasing of ZnSe content. XRD has shown that samples have ZnSe, SnSe, Se and Sn phases. It was found the inversion of the conductivity type. Samples fabricated at 500 °C and 550 °C performed p-type of conductivity. While samples fabricated at 600 °C shown n-type conductivity.

Key words: $Zn_XSn_{1-X}Se$ films, X-ray, morphology, grain size, conductivity.

1. Introduction

Currently, 85% of photovoltaic market are made using crystalline or multi-crystalline wafer silicon. However, producing power with these cells remains expensive compared to conventional power generation. In order to reduce production costs, thin film solar cells have been developed especially those based on cadmium telluride and on copper indium gallium diselenide. Despite the excellent success of these cells in recent years (22.1% [1] -23.35 % [2] efficiency respectively), problems remain: in the former cells, there is a particular need to control disposal after use due to the presence of cadmium; in the latter cells, the scarcity of indium supply and the high material cost of indium and gallium impelled researchers to look for an alternative photovoltaic material.

Novel low cost and high efficiency zinc and tin selenide ($Zn_xSn_{1-x}Se$) thin film solar cells are without these drawbacks. However, there is no information in world literature regarding this new material. This compound has excellent photovoltaic properties: i) the band gap can be varied in the very wide range of (0.9 – 2.7) eV, which is suitable for single junction thin film solar cells with optimum direct energy band gap of 1.45 eV and double junction cells with band gaps of E_{g1}=1.0 eV and E_{g2}=1.7 eV for photovoltaic solar energy conversion with the efficiencies of (20-25)% and (30-35)% respectively, ii) absorption coefficient is $10^4 – 10^5$ cm^{-1}, which means that an absorber thickness of (0.5-1.0) µm is enough to fabricate high efficiency cells, iii) it consists of abundant elements and it can be made either *n*-type or *p*-type conductivity.

Earlier, we had discussed characteristics of SnSe films in [1]. We have fabricated $Zn_xSn_{1-x}Se$ (ZTS) films for the first time. The effect of the substrate temperature on morphology, structure and conductivity of ZTS films is discussed in this paper.

2. Experiment

Samples were fabricated by chemical molecular beam deposition method at atmospheric pressure in hydrogen flow [2]. ZnSe and SnSe powders with 99.999 % purity were used as precursors. The temperature of precursors varied in the range of (850 – 950) °C. Films were deposited at substrate temperatures of (500 – 600) °C. Borosilicate glass was used as a substrate. We have studied ZTS films by EDS, XRD, SEM and four probe method. The crystal structure of films were investigated by XRD measurements using a "Panalytical Empyrean" diffractometer (Cu Kα radiation, λ=1.5418 Å) with a wide-angle measurements of 2θ in the range of (10–90)° with a measurement steps of 0.01°. The experimental results were studied using the 'Joint Committee on Powder Diffraction Standard' (JCPDS, № 15-0861 for SnSe films). Morphological and chemical composition of the samples were investigated using a scanning electron microscope (SEM-EVO MA 10) and an energy-dispersive X-ray spectroscopy (EDX, Oxford Instrument - Aztec Energy Advanced X-act SDD) at an electron acceleration voltage of 15 kV, respectively. To perform electrical measurements, ohmic contacts were realized by vacuum deposition of silver on the films. The conductivity of films was measured by van der Pauw method. The type of conductivity of the samples was determined by thermoelectric effect. The thickness of the films was determined using micro-interferometer MII-4.

3. Results and discussion

At the evaporation temperature ZnSe and SnSe powders transfer into the vapor phase:

$$ZnSe_s + SnSe_s + H_2 = ZnSe_g + SnSe_g + H_2 \qquad (1)$$

Then ZnSeg and SnSeg dissociate into Zng, Sng and Seg:

$$ZnSe_g + SnSe_g + H_2 = Zn_g + Sn_g + Se_{2g} + H_2 \qquad (2)$$

Se_{2g} reacts with hydrogen and hydrogen selenide is formed:

$$Se_{2g} + H_2 = H_2Se_g \qquad (3)$$

Zn and Sn atoms and H2Se molecules reach the surface of the substrate and as a result of their interaction the ZTS films is formed:

$$Zn_g + Sn_g + H2Se_g = Zn_xSn_{1-x}Se_s + H_2 \qquad (4)$$

We controlled ZTS films composition by changing the vapor phase mixture of $(ZnSe)_x(SnSe)_{1-x}$. The dependence of films composition on the vapor phase mixture is shown in Fig.1. It is seen that this dependence has almost linear character. It was observed that the composition of ZTS films strongly depends on the substrate temperature. As seen from Fig.2, the composition of ZTS films moves to ZnSe side with the substrate temperature.

It shows that the sublimation of Zn atoms increases with the substrate temperature despite high vapor pressure of Sn in comparison with Zn. While Sn vapors being carried away from the deposition zone by hydrogen. Content of Sn in ZTS increases with decreasing the substrate temperature.

X-ray diffraction patterns of ZTS films fabricated at different substrate temperatures are shown in Fig.3. The spectra were obtained by scanning 2θ in the range 20–60°, with a grazing angle equal to 1.5°. We can see from the diffraction patterns that the peaks intensity increases as the composition x increases and this is due to the growth of material involved in the diffraction process. Moreover, peak (400) moves to high theta side with increasing Zn content in ZTS. The samples had orthorhombic and cubic structures depending on substrate temperature. XRD has shown that samples have ZnSe, SnSe, Se and Sn phases as well.

SEM pictures (Fig.4) have shown that samples have polycrystalline structure. The grain size varied in the range of (2-15) µm. The grain size of samples increased from (2-5) µm to (15 -20) µm for substrate temperatures of 500 °C and 550 °C respectively. While, at substrate temperature of 600 °C the grain size decreased up to (3-5) µm, possibly, because of increasing of ZnSe content.

Fig. 5 shows the absorption spectra of three ZTS films fabricated at different precursors temperatures in the wavelength range of 300–1500 nm. The band gap of the films was calculated by plotting (αhν)2 against hν. The band-gap values were determined from the intercept of the straight-line portion of the (αhν)2 against hν graph on the hν axis. The band gap increased with ZnSe precursor temperature from 1.0 eV to 2.1 eV. This is due to by the fact that the band gap of ZnSe is high (2.7 eV) than the band gap of SnSe (1.0 eV).

Electrical parameters of ZTS films are presented in Table 1. It is seen that the conductivity of samples decreases with the substrate temperature. The conductivity of samples fabricated at 500 °C and 550 °C were 100 and 25 (Ohm x cm)$^{-1}$ respectively. The conductivity of the sample fabricated at the substrate temperature of 600 °C significantly increased up to 10^{-6} (Ohm x cm)$^{-1}$. It is caused owing to increasing the band gap of ZTS films with the composition x. Moreover, we have observed the inversion of the type of conductivity. The samples fabricated at the substrate temperatures of 500 °C and 550 °C had p-type of conductivity. While the sample fabricated at the substrate temperature of 600 °C performed n-type of conductivity.

Conclusion

The ZTS films have been fabricated by chemical molecular beam deposition in atmospheric pressure hydrogen flow at substrate temperatures of 500 °C, 550 °C and 600 °C for the first time. XRD, SEM, optical and electrical properties were studied. The composition of ZTS films moves to ZnSe side with the increasing the deposition temperature. The samples had cubic and orthorhombic structure with the grain size of 2-20 µm. The optical band gap increased as the composition of ZTS moves to ZnSe side. We observed the inversion of the type of conductivity from p-type to n-type and the decreasing the conductivity with x.

Acknowledgement

This work was supported by the grant F2-003 of the Basic Research Foundation of the Uzbekistan Academy of Sciences.

References

1. http://www.pv-magazine.com/news/details/beitrag/first-solar-sets-new-cadmium-telluride-thin-film-cell-efficiency-record-at-22.1_100023341/#ixzz415kIS7YW.
2. http://www.renewableenergyworld.com/rea/blog/post/2014/03/two-thin-film-solar-efficiency-records-broken-this-week?cmpid=WNL-Wednesday-March5-2014.

3. T.M. Razykov, G.S. Boltaev, A. Bosio, B. Ergashev, K.M. Kouchkarov, N.K. Mamarasulov, A.A. Mavlonov, A. Romeod, N. Romeo, O.M. Tursunkulov, R. Yuldoshov. Characterisation of SnSe thin films fabricated by chemical molecular beam deposition for use in thin film solar cells, Solar Energy 159 (2018) pp. 834–840.
4. T.M.Razykov, Chemical molecular beam deposition of II-VI binary and ternary compound films in gas flow, Applied Surface Science, 1991, V.48/49, pp.89-92.

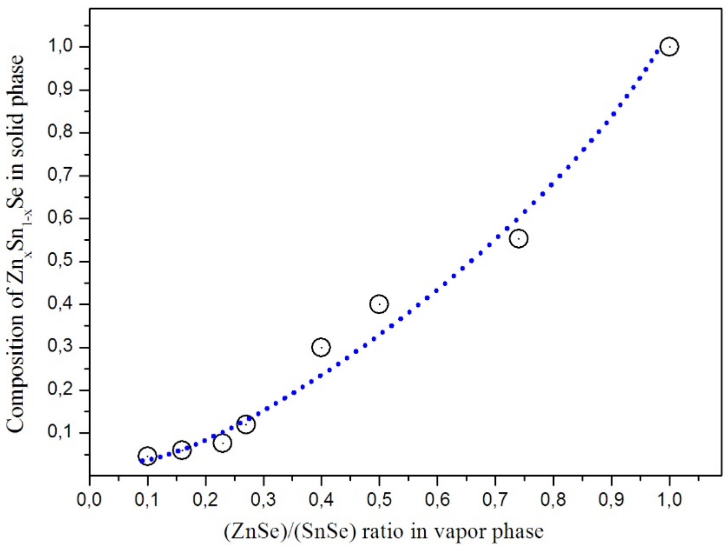


Fig.1 The dependence of films composition on the vapor phase mixture

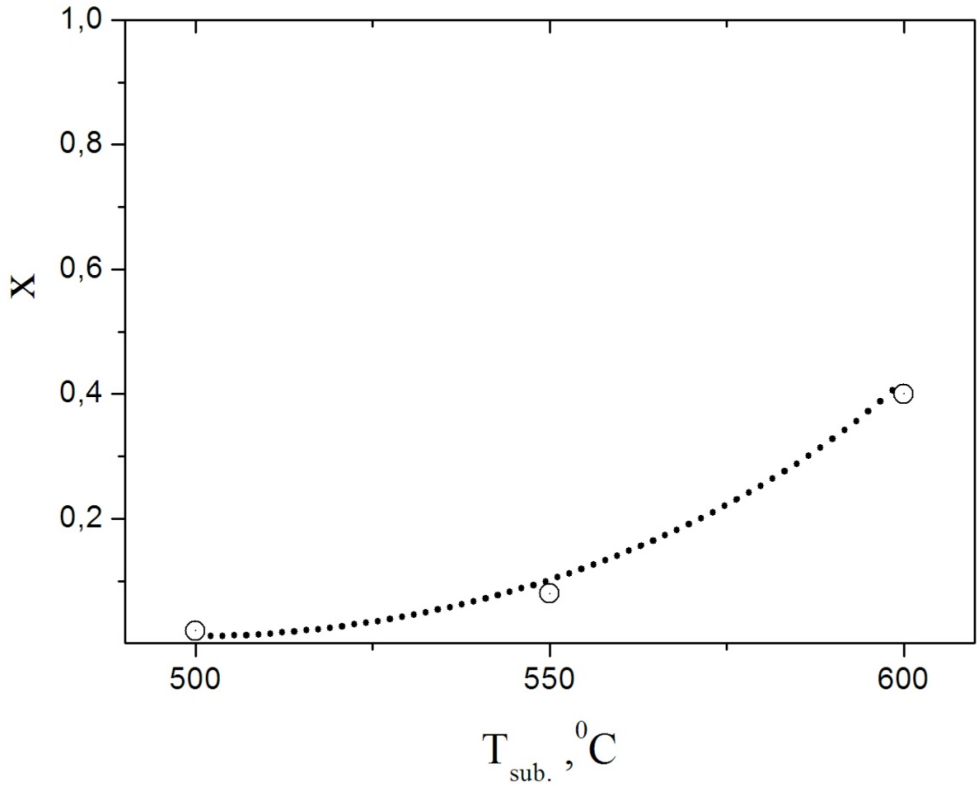


Fig.2 Dependence of the composition of ZTS films on substrate temperature.

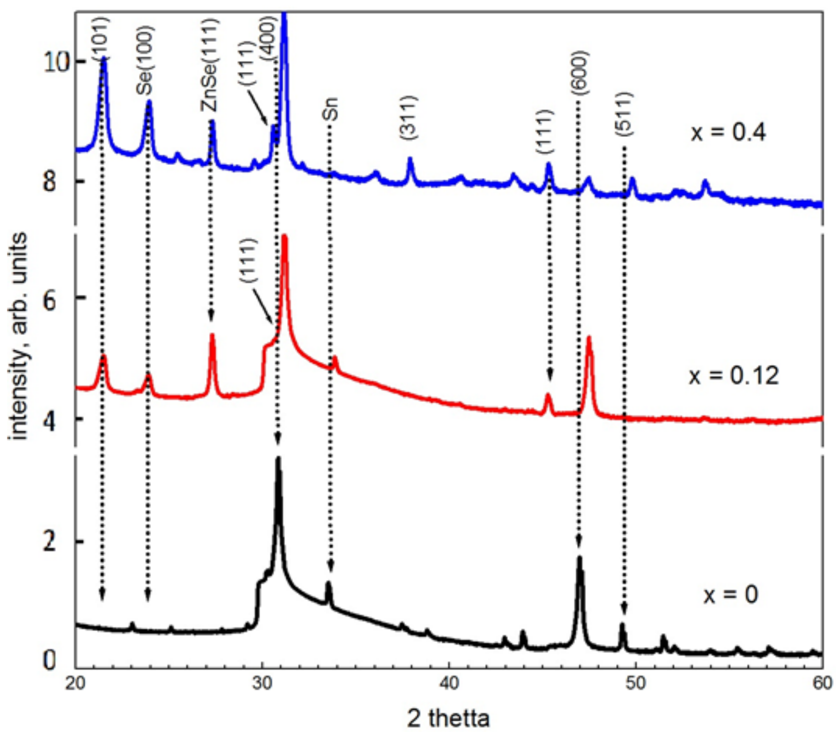
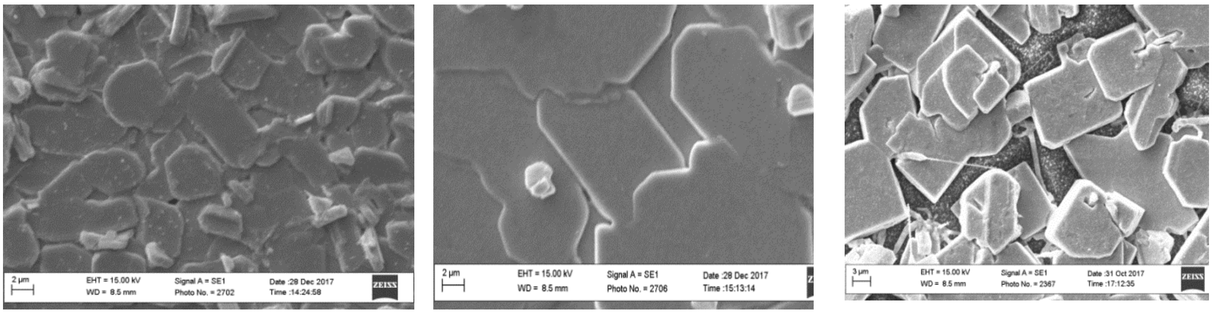


Fig.3 X-ray diffraction patterns of ZTS films with different compositions.



a b c

Fig.4 SEM images of ZTS films fabricated at different substrate temperatures: а) Ts= 500 °C; б) Ts= 550 °C; и в) Ts= 600 °C.

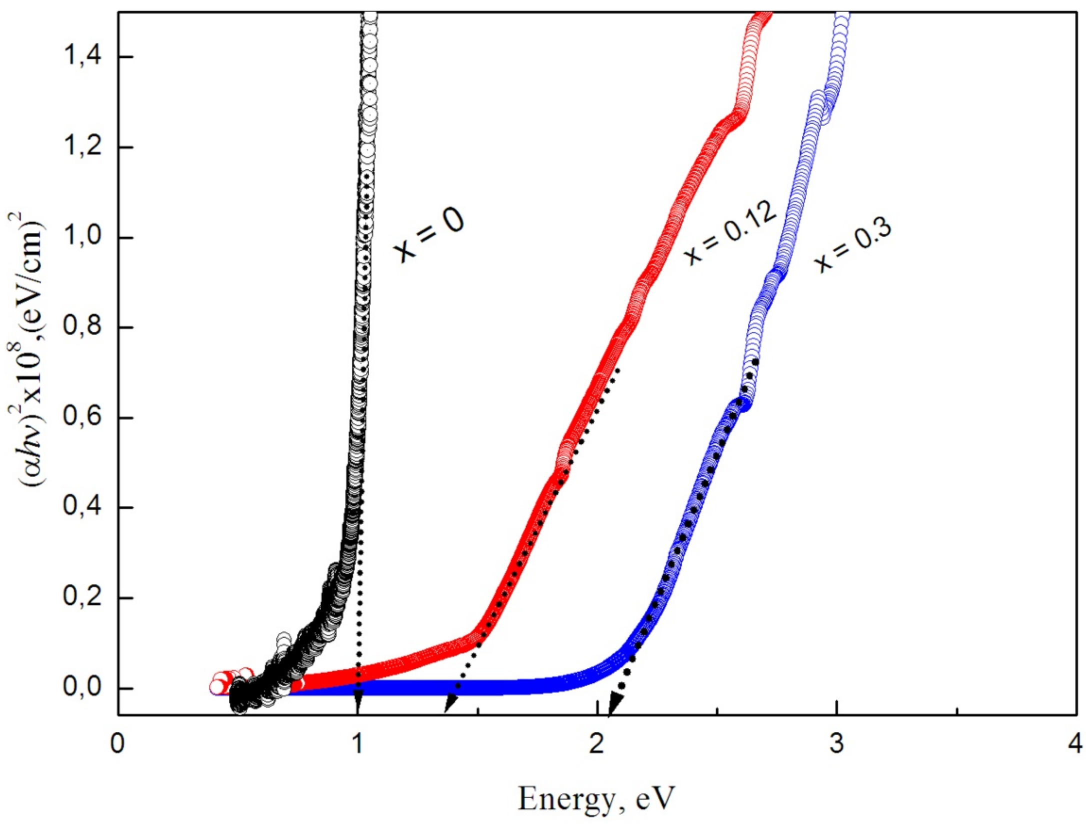


Fig.5 The absorption spectra of ZTS films with different compositions fabricated at substrate temperture of 550 °C.

Table 1 Electrical parameters of ZTS films.

Тп(°С)	Пленки, осажденные из соединения ZnSe и SnSe стехиометрического состава			
	Состав пленок	σ (Ом·см)$^{-1}$	$E_{активации}$ (эВ)	Тип пров-ти
500	x= 0.026	100	0 .02	p
550	x= 0.08	25	0.04	p
600	x= 0.4	1x10^{-6}	0.22	n