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Investigation of Structural and Optical Properties of CdS, CdZnS and CdSnS thin films deposited by Chemical Spray Pyrolysis Technique

Sibel Morkoç Karadeniz,
University of Erzincan, Erzincan, Turkey,
Demet Tatar
University of Atatürk, Erzurum, Turkey
Tuba Kılınç, Burcu Bozkurt Çırak, Çağrı Çırak, Ali Ercan Ekinci
University of Erzincan, Erzincan, Turkey
and Mehmet Ertuğrul
University of Atatürk, Erzurum, Turkey

Abstract

In this study, CdS, CdZnS and CdSnS films on glass substrates have been deposited with Chemical Spray Pyrolysis technique for same experimental conditions. Similar films in terms of molarity and volume ratio have been exposed to annealing process at 400 °C for 2 hours. The thin films have been characterized by X-Ray diffractometer for structural; Scanning Electron Microscopy for morphological; UV-Vis spectrometer for optical characteristics. When structural and surface characteristics have been evaluated, it can be seen surfaces that arranged by nanoplates for CdSnS thin film, consisted by pin holes for CdZnS thin film, formed by nanosized grains for CdS thin film. Moreover, hexagonal crystal structure which has different orientations for all of the films. When the optical characteristics have been evaluated, energy bandgaps have been changed with Zn or Sn doped.

Introduction

With solar cells, n type CdS thin films that has 2,48eV bandgap at room temperature and that is one of the semiconductor compound II-IV have many application areas such as optical detectors, dosimeters, field-effect transistors, laser materials and optoelectronic devices [1,2]. CdS thin films are preferred mostly in solar energy systems because of its high conductivity and low resistance [3]. ZnS compound that is among the II-IV group semiconductors and has an energy bandgap 3.6-3.7 eV at room temperature have suitable potential for electroluminescence devices, solar cells and other optoelectronic device applications [4]. Being an IV-VI group compound p type semiconductor, SnS having orthorhombic crystal structure and 1.2 and 1.5 eV direct and indirect bandgap respectively and stands out in photovoltaic device applications as non-toxic material and found largely in nature [5].

Hetero-structure based thin films consisted of II-VI group compounds are rather suitable for use in photovoltaic devices because of its high optical absorption coefficient [6].In addition, it has been stated in literature that $Cd_{1-x}Sn_xS$ structures haven't been studied much in literature and actually they are suitable structures for solar cells [7].

Cadmium Zinc Sulfide ($Cd_xZn_{(1-x)}S$) have been reported in the literature as an ideal alternative material for solar cells with an energy bandgap approximately 3.5 eV and bigger than ZnS thin films that has approximately 3.7 eV bandgap and bigger than CdS thin films which has approximately 2.4 eV bandgap [8]. It is known that CdZnS nanoparticles are suitable for short wavelength laser applications beyond blue or UV area [9]. Nonetheless, ZnCdS films has been considered more suitable for solar cells as it is more appropriate to thin films including solar cells with higher energy bandgap from CdS and it can be adjusted in compound and size and also it has absorption coefficient in blue or UV area, it allows the increase in photocurrent which provides a match in the electron bonds of window and the absorbed substance [9-11]. The use of $Cd_{1-x}Zn_xS$ instead of CdS can lead to an increase in photocurrent by providing a match in the electron affinities of the two materials [12].

In the scope of this study, CdS thin films which are used in solar cells applications have been deposited by using the Chemical Spray pyrolysis technique that is an easy and cheap solution based deposition technique; the effect of Zn or Sn doped on its structural and optical characteristics have been examined and a comparison has been made.

CdZnS and CdSnS structures which have different optical and structural characteristics doped by Zn and Sn separately in the same volume ratio to CdS have been formed.

Experimental

In this study, CdS thin films doped by Zn and Sn separately on glass substrate have been deposited with using the Chemical Spray Pyrolysis technique. CSP is an easy and cheap that is based on spraying the solution to the surface under a certain substrate temperature and that can be obtained good crystal structures. In this study, substrates have been cleaned with acetone for 20 minutes and with methanol for 20 minutes in ultrasonic cleaner and dried at 60 ℃ in an oven. Moreover, all solutions have been prepared as 0.05 Molar. Prepared solutions have been sprayed on the substrate at 275-300 ℃ as 1-2 ml per minute. Air has been used as the carrier gas. The substrates have been controlled continuously by the temperature probe.

The temperature during the process has been observed to change between 275-300 ℃ because of the cooling on the surface after spraying on. The films obtained later have been exposed to annealing process at 400 ℃ for 2 hours. The details of experimental parameters have been added in Table 1. The details of CSP system has been given in reference [13].Structural, optical and surface characteristics of deposited thin films have been evaluated and compared.

Table 1.The details of experimental parameters.

$CdCl_2$:Thiourea Volume ratio (1:1)	$SnCl_2$:Thiourea, $ZnCl_2$:Thiourea Volume ratio (1:1)
50 ml	0 ml
30ml	20ml

Results and Discussion

XRD patterns of CdS, CdZnS and CdSnS thin film represented as Sample A, sample B and Sample C given in Figure 1. When XRD spectrum of Sample A has been evaluated, it has been seen peak of the (002) hexagonal plane is the sharpest peak. When the XRD spectrum of Sample B has been evaluated, according to Sample A, there has been a change in peak intensity and hexagonal (001) peak has been the sharpest peak. [8].

As shown in Figure 1, preferred orientation has changed towards hexagonal (011) plane when XRD spectrum of Sample C has been evaluated. The details of the XRD results are given in Table 2.

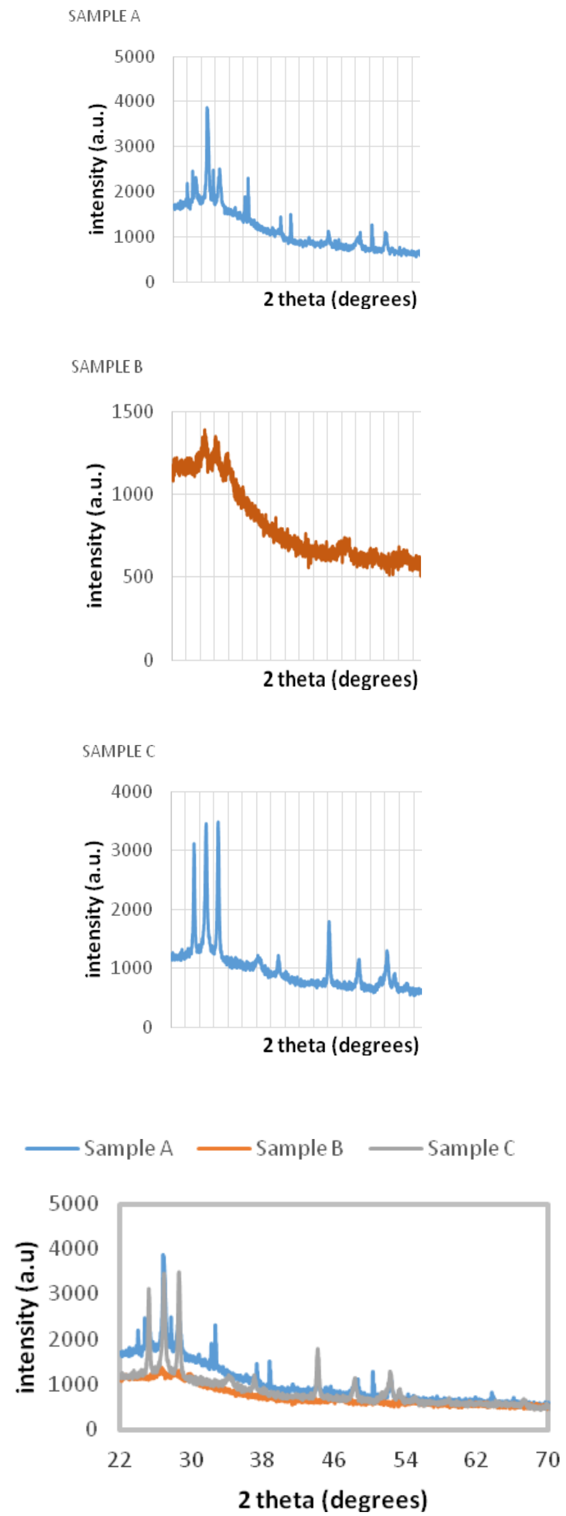

Figure 1. XRD patterns of Sample A, Sample B and Sample C and XRD relative intensity spectrum of three films together.

Table 2. XRD data of Sample A, Sample B and Sample C.

Reference[14]: ICSD collection card :154188			Sample A		
2 Theta (degrees)	d –spacing (Å)	h k l indices	2 Theta (degrees)	d -spacing (Å)	D (grain size nm)
25.115	3.5429	(0 1 0)	25.223	3.5289	37.04
26.828	3.3205	(0 0 2)	26.800	3.3265	115.18
28.532	3.1259	(0 1 1)	28.599	3.1214	26.21
37.077	2.4228	(0 1 2)	37.280	2.4120	219.1
44.244	2.0455	(1 0 0)	44.090	2.0540	49.66
48.449	1.8773	(0 1 3)	48.648	1.8716	70.40
52.502	1.7415	(1 1 2)	52.276	1.7500	33.22
Reference[15] : ICSD collection card :620384			Sample B		
2 Theta (degrees)	d –spacing (Å)	h k l indices	2 Theta (degrees)	d -spacing (Å)	D (grain size nm)
26.645	3.3429	(0 1 0)	26.706	3.3381	15.07
28.263	3.1550	(0 0 2)	28.208	3.1637	15.12
30.232	2.9540	(0 1 1)	29.951	2.9834	11.36
47.046	1.9300	(1 0 0)	46.706	1.9448	11.95
Reference [14] : ICSD collection card : 154188			Sample C		
2 Theta (degrees)	d –spacing (Å)	h k l indices	2 Theta (degrees)	d -spacing (Å)	D (grain size nm)
25.115	3.5429	(0 1 0)	25.206	3.5330	82.8
26.828	3.3205	(0 0 2)	26.875	3.3176	47.4
28.532	3.1259	(0 1 1)	28.567	3.12477	55.2
37.077	2.4228	(0 1 2)	37.000	2.4297	38.1
44.244	2.0455	(1 0 0)	44.091	2.0540	69.2
48.449	1.8773	(0 1 3)	48.335	1.8831	39.6
52.502	1.7415	(1 1 2)	52.277	1.7400	40.3
53.493	1.7116	(0 2 1)	53.299	1.71880	33.4

In Figure 2, SEM microphotographs of Sample A-B-C are shown. Each photograph has been taken in high vacuum condition in 40.000 and 80.000 magnifications. When the SEM photographs of CdS thin films are evaluated, it is seen that the surface has high roughness rate and includes grains at different sizes. The surface changes with Zn added to the structure at 40% ratio and morphology of the structure includes different sized pin holes that cover the surface completely. Surface grain has changed to laminated plates with Sn at 40% ratio added to the structure. Plate structures on surfaces show a homogeneous distribution. When EDX spectrums in Figure 3 have been evaluated, it can be seen that there is zinc peak intensity on surface doped by Zn at 40% ratio and zinc peak is at the top level. Besides, Cd peak has been sharper than Sn peak with doped Sn at the same ratio.

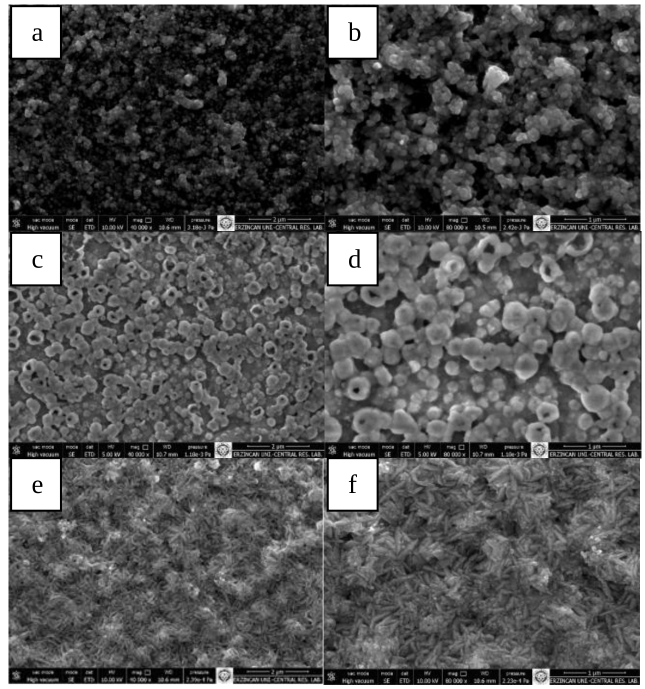

Figure 2. SEM images of a-b) Sample A, c-d) Sample B, e-f) Sample C

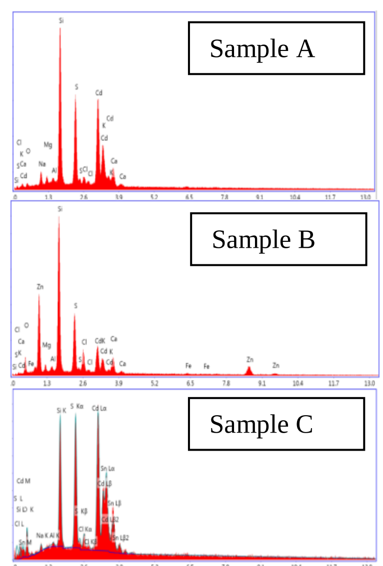

Figure 3. EDX spectra of Sample A, Sample B and Sample C

In Figure 4, UV-vis spectra of Sample A-B-C are shown. Looking at the transmittance graphics of three structures in figure 4a, it is seen that the highest transmittance is obtained in CdZnS film. The transmittance of CdSnS film that is Sn doped at the same ratio is the lowest. As seen in figure 4b, energy bandgap of CdS has been found in line with literature as 2.4eV corresponding to energy bandgap- the square of absorption coefficient graphic obtained with transmittance results. Whereas the bandgap increases with the zinc added to the structure and reaches a value of > 3 eV and energy bandgap becomes < 2.5 and bandgap of CdS by adding Sn.

It is seen that, lower or higher bandgaps can be obtained with Sn and Zn added to CdS structure by changing the proportional volumes and it is thought that bandgap can be controlled at will. Moreover, a CdZnS thin film which has the most transmittance and highest bandgap is thought to be the suitable structure to others for solar cells.

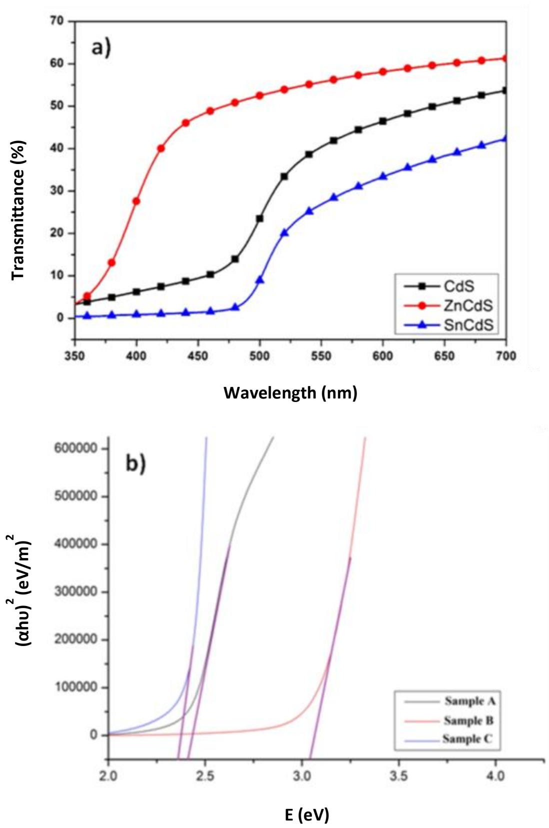

Figure 4. a) Spectral Transmittance of the Samples, b) Plot of $(\alpha h\upsilon)^2$ versus E for all of the Samples

Conclusions

In this study, the differences between structures have been presented by examining the optical, structural and surface characteristics of CdSnS and CdZnS films created by Zn and Sn doped at the same volume ratio and molarity to CdS structure which has commonly used in solar cells applications. CdS, CdZnS and CdSnS thin films have been deposited by using the Chemical Spray Pyrolysis technique that is an easy solution based technique. At the end of both doping, different surface structures have been obtained with Zn and Sn ions taking the place of Cd which has +2 valances in the structure. According to the XRD results, preferred orientation has been changed when crystal structure is generally hexagonal structure for three films. When the optical results have been evaluated, CdZnS structures are thought to have the highest bandgap and transmittance and it is more suitable for solar cell applications compared to CdSnS and CdS structures.

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