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Influence of Sn Doping on Cds Thin Film Grown by Ultrasonic Spray Pyrolysis

Zeynep Deniz Eygi *, *Barbaros Demirselçuk and Vildan Bilgin*

Department of Physics, Çanakkale Onsekiz Mart University, Turkey.

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Abstract: Sn doped CdS thin films were grown onto glass substrates through Ultrasonic Spray Pyrolysis technique. The effect of the Sn dopant on the optical, structural and electrical properties of CdS films was investigated. Undoped and doped CdS films presented a hexagonal structure. The band gap of each film was calculated as 2.43 eV by using transmission spectra. The electrical analysis proved the improvement in resistance by increasing Sn dopant atoms in CdS lattice. All the CdS:Sn films were evaluated as a potential window material for heterojunction solar cells.

Keywords: CdS:Sn thin films, ultrasonic spray pyrolysis, XRD, AFM

1 Introduction

Cadmium sulfide (CdS) thin film is one of the attractive materials in photovoltaic technology due to its wide band gap energy, stability and superior optical and electrical properties. CdS thin films have been broadly used as a window layer to form high efficiency heterojunction solar cells [1-5]. In the fabrication of a window layer for a solar cell, homogeneity, stability, uniformity, low electrical resistivity and high optical transmittance are primarily desirable [6,7]. Spray pyrolysis technique meets the requirements of good quality polycrystalline CdS thin films with high growth rate, thickness controlling, and reproducibility at relatively low deposition temperatures [8].

Electrical, optical and structural properties of CdS thin films mainly depend on processing conditions. However adjusting process parameters cannot be sufficient in order to achieve the required films. Adding dopant materials is an efficient way in achieving desired film properties by means of reducing the electrical resistivity and adjusting optical properties. In spray pyrolysis, a variety of metals can easily be introduced into the spray solution to obtain doped CdS thin films. Doped CdS films; prepared by various deposition techniques; with different metals such as Cu [9, 10], Ga [11], Er [12], Co [13], Mn [14], Al [15], In [16] and Sn [17-21] have been studied. Choosing the doping material allows to change the conductivity type of the CdS thin films. Another important point in choosing doping material is the comparable atomic size of impurity atoms and host atoms [17]. In this point of view, Sn is a promising metal in obtaining n type CdS films because Sn atoms can easily substitute Cd in the lattice due to their similar atomic sizes. However, there is a few reports on Sn doped CdS films grown by spray pyrolysis. In this work we submit the structural, optical and electrical properties of Sn (3-15 vol. %) doped CdS films grown via ultrasonic spray pyrolysis technique.

2 Experimental

2.1 Film Preparation

Table 1: The volume values for aqueous spray solution and the thickness of the CdS:Sn films

Sn volume percentage	**Film Thickness (nm)**	**Tin chloride [$SnCl_2$]**	**Cadmium Chloride [$CdCl_2.2H_2O$]**	**Thiourea [CH_4N_2S]**
		Volume (ml)		
0%	250	0	75	75
3%	300	4,5	72,75	72,75
6%	428	9	70,5	70.5
9%	416	13,5	68,25	68,25
15%	461	22,5	63,75	63,75

CdS:Sn thin films; with different Sn doping concentration (3,6,9,15 vol %); were coated onto pre-cleaned microscope glass (1cm×1cm) by using an ultrasonic spray pyrolysis system at a substrate temperature of 300±5°C. The spray solutions were prepared by mixing the appropriate volumes

*Corresponding author E-mail: zeynepdeniz@gmail.com

of cadmium chloride (0.025 M), thiourea (0.025 M) and tin chloride (0.01 M) dissolved in de-ionized water. In this study, the solution ratio of Cd:S was kept constant as 1:1 and Sn ratio was varied as summarized in Table1. The 150 ml solution was sprayed through ultrasonic nozzle using air as carrier gas with a pressure of 10^5 Pa during 30 min. with a flow rate of 0.5 ml.min^{-1}. The spray mixture was stirred by a magnetic stirrer throughout the coating process and the distance between the spray nozzle and the substrate was fixed at 35 cm.

2.2 Characterization Techniques

The structural properties of the CdS:Sn films were analysed by X-Ray diffraction (XRD). The XRD patterns were recorded by using 'Rigaku Ultima IV' X-ray diffractometer with CuKα radiation (λ = 1.5408 A˚) in the 2θ range of 10˚ to 80˚ at 40 kV and 30 mA. The optical transmittance spectra of the thin films were measured by using a Shimadzu UV-2550 (double beam, 190-900 nm) spectrophotometer. The surface characterization of the films was conducted by using atomic force microscope (AFM, Park Systems XE100). OPT-S9000 Spectroscopic Ellipsometer was used to measure the film thickness. Compositional study of the films was analyzed by Scanning Electron Microscopy (SEM) attached with an X-ray spectroscopy (EDX). The electrical properties of the films were evaluated from the I–V characteristics measured by means of Keithley 2400 source meter at room temperature.

3 Results and Discussion

3.1 Structural Characteristics

The structural properties of the undoped and Sn doped CdS thin films analyzed by XRD are shown in Fig.1

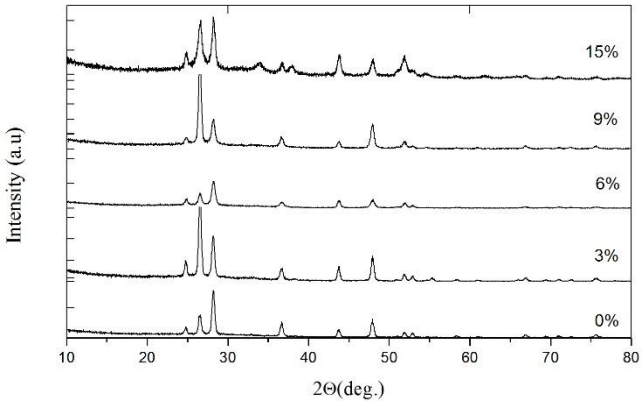

Fig.1. XRD spectra obtained from CdS:Sn films with varying vol % of Sn.

From Fig.1 it can be seen that all films show the diffraction peaks at around 24.8˚, 26.6˚, 28.1˚, 36.7˚, 43.7˚, 47.8˚, 51.8˚ which correspond to the diffraction from (100),(002),(101),(102), (110), (103), (112) planes for hexagonal structure of polycrystalline CdS, respectively. The average crystallite size of the each sample is calculated with the help of the Scherrer's formula (1).

$$D = \frac{0,94\lambda}{\beta Cos\theta} \quad (1)$$

Where D is the crystallite size, β is the FWHM of the most intense XRD peak and λ is the X-ray wavelength. The lattice spacing and crystallite size for all samples are summarized in Table 2.

Table 2: The space between the planes in the atomic lattice (d) and the crystallite size (D) of undoped and Sn doped CdS thin films.

Sample	d (A˚)	D (A˚)
CdS	3.16	219
CdS:Sn (3%)	3.20	222
CdS:Sn (6%)	3.16	171
CdS:Sn (9%)	3.35	222
CdS:Sn (15%)	3.16	185

From Table 2, slight changes in lattice spacing are observed due to similar atomic size of Sn and Cd atoms. However, when Sn doped CdS thin film at the volume concentration of 6 % and 15%, the FWHM of the peaks are increased and hence grain size decreases. This indicates that the crystallinity of the CdS:Sn films reduces. It should be noted that, at the volume concentration of 15 %, impurity phases were occurred due to large Sn concentration.

The film thickness on the other hand enhanced with increasing Sn volume concentration in the spray solution while solution volume and spraying time was kept same for all samples. This can indicate that Sn atoms occupy the interstitial site in the lattice and hence lead thicker films on the substrate. Table 1 shows the variation in film thickness as a function of Sn volume concentration in spray solution. To confirm the existence of Sn in the CdS films, the elemental composition of the samples was investigated by EDX measurement. Fig. 2 represents the EDX spectra and quantitative results of CdS:Sn (15 vol% Sn) thin film. According to EDX result the CdS:Sn (15 vol% Sn) film contained 17.5 at.% of Sn.

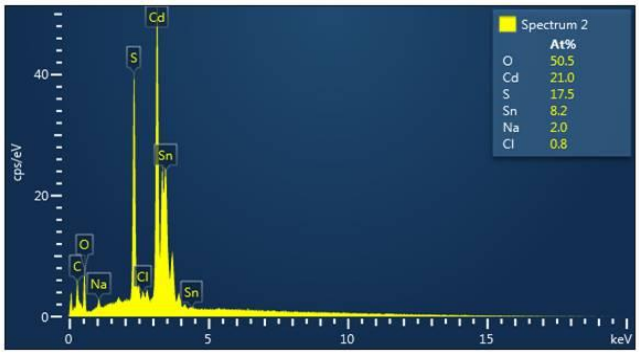

Fig.2. EDX micrograph of CdS:Sn by the 15% Sn volume percentage thin film on glass substrate.

3.2 Optical Characteristics

The absorbance and transmittance spectra for the films are shown in Fig.3a and Fig.3b, respectively.

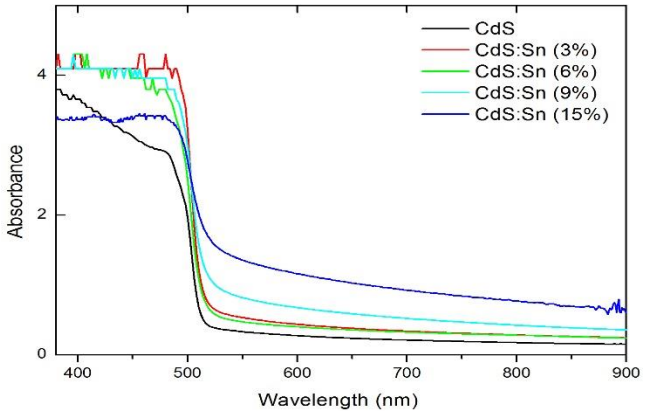

Fig.3a. The optical absorbance spectra of the CdS:Sn thin films.

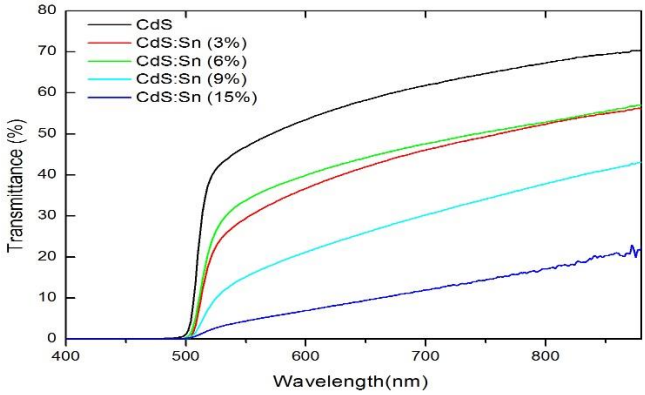

Fig.3b. The optical transmission spectra of the CdS:Sn thin films.

From the absorbance spectra (Fig.3a), it can be seen that the absorbance decreases with the increase in wavelength and a sharp decrease is observed at the wavelength ~550 nm. As seen from Fig.3b, the optical transmissions of the films are approximately between 20-70% in the range of 600-900 nm and transmission decreases with increasing Sn doping concentration. This can probably be caused by disorder in the crystal due to the incorporation of dopant atoms. The band gap energies (E_g) of the films were determined by plotting the $(\alpha h\nu)^2$ versus ($h\nu$) graph. The E_g values were obtained between 2.43-2.44 eV. Low absorbance and high transmittance at the wavelength region of ~500–900 nm makes CdS:Sn films appropriate window layer for photovoltaic applications.

AFM images of the films with a scanning area of $10\times10\mu m^2$ are shown in Fig.4 (a-e). It is observed that the surface morphology of all the films has a fine microstructure without voids, pinholes and cracks. However, increasing Sn volume concentration caused more aggregation particles on the film surface.

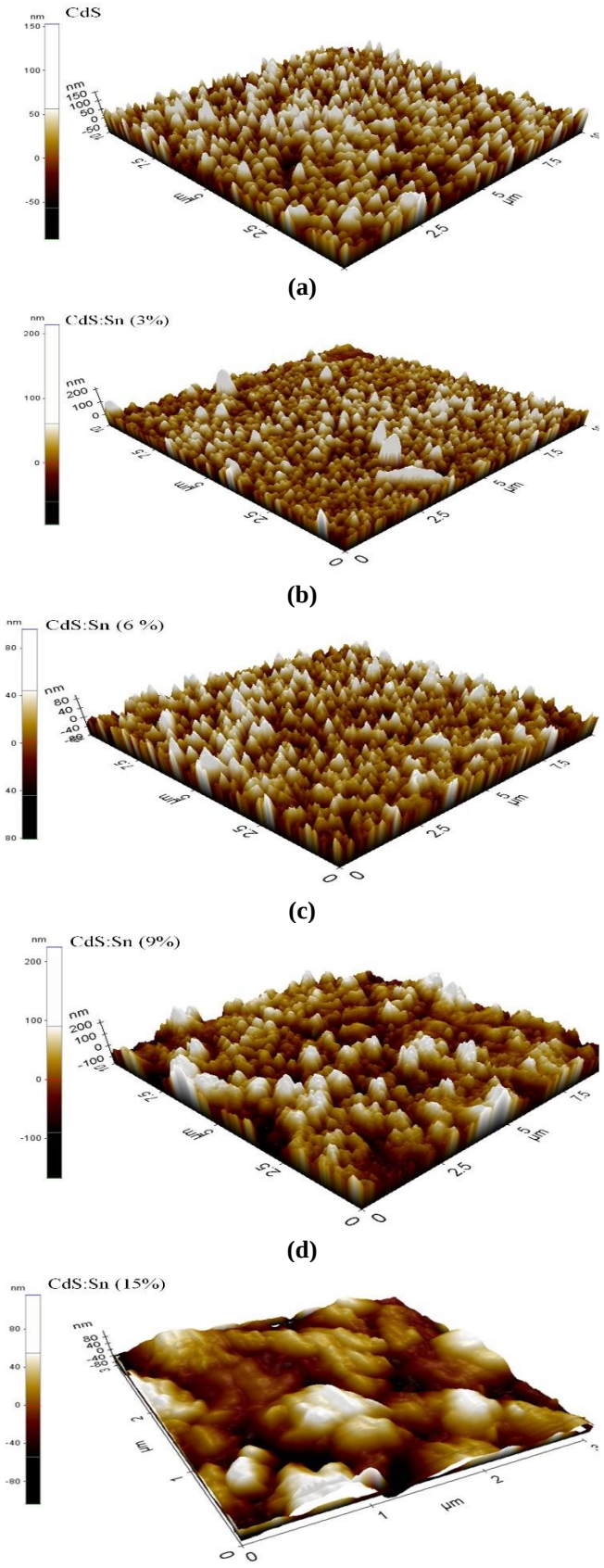

Fig.4a-e. AFM images of the CdS:Sn thin films

3.3 Electrical Characteristics

The I-V measurement of CdS:Sn thin films were performed in the voltage range of 0-20 V at room temperature. The variation in resistance of the films as a function of Sn volume percentage is shown in Fig.5.

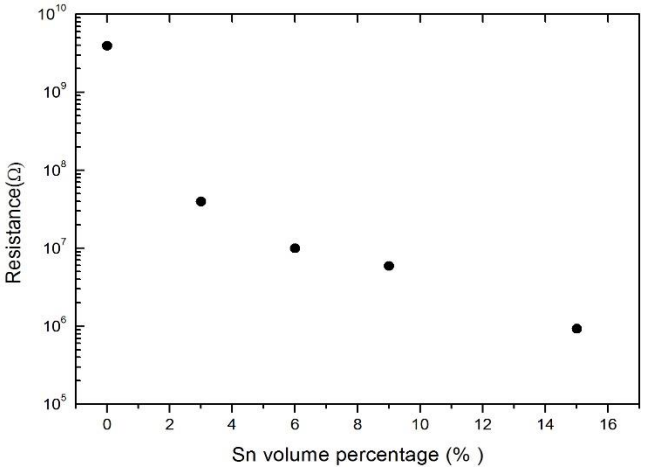

Fig.5. Resistance values of the CdS:Sn thin films.

4 Conclusion

CdS thin films, doped with various concentration of Sn was grown successfully via ultrasonic spray pyrolysis technique. All films represented hexagonal structure of polycrystalline CdS with the band gap values of 2.43-2.44 eV. No considerable change in the lattice parameters was observed with the introduction of Sn atoms. However, increasing Sn atoms caused deteriorating of crystalline quality. Increasing Sn atoms yields higher growth rate during deposition.The transmission decreased from 70% without doping to the ~10% with higher Sn doping concentration. The resistivity of the films decreases with increase in Sn concentration, and the film with 15 vol% Sn doping showed a minimum resistance. By considering structural, optical and electrical properties of the films CdS:Sn (3 vol% Sn) represented most suitable properties as window layer for solar cells.

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