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Structural and Optical Properties of Cu2Zn1-xCdxSnS4 Thin Film as an Absorber Material for Solar Cell

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***Abstract*-- $Cu_2Zn_{1-x}Cd_xSnS_4$(CZCTS) film is successfully prepared by chemical spray pyrolysis on glass substrate at 340°C,where x= 0 and 0.2. CZCTS is considered sa one of the most promising light absorbing material for low cost and high efficiency thin film solar cell. X-ray diffraction characterization results reveal that the layer is indexed to a multi phase polycrystalline with preferred orientation on the (112),(220),(312) planes thereby confirming the kesterite structure of Cu_2ZnSnS_4 .AFM morphology analysis by atomic force microscopy reveals that the grain size of the prepared thin film is approximately (90)nm ,with a surface roughness of (1.96,1.85)nm and root mean square of (2.33,2.25)nm for x=0 and 0.2 . the direct energy gap (E_g) in (1.7)eV and (1.66) for x=0 and 0.2, respectively, is measured by UV-vis spectrophotometry , and these values are close to the optimum value for semiconductor materials as an absorber in solar cells.**

***Keywords* - Thin Film, Structural and Optical , CZCTS**

I. INTRODUCTION

Studies on Cu2ZnSnS4 (CZTS) and related compounds Cu2ZnSn(S,Se)4 are increasing because they are some of the most promising materials as an absorber layer in thin film solar cells[1-5]. CZTS is a p-type quaternary compound semiconductor with a Kesterite crystal structure having a high absorption coefficient in the order of 104cm-1 and a direct band gap of approximately 1.5eV, which is the optimal value required for a solar cell absorber layer. these properties suggest that CZTS is a potential photovoltaic materials. Controlling the chemical composition is one of the key factors that can improve the e efficiency of thin film solar cell. Several methods have been used to fabricate desired thin-film solar cells based on CZTS thin films. [2,6] . Altosaar et al.[2] found the best solar cell based on Cu2Zn0.8Cd0.2SnSe4. Deposition technologies for CZTS that have been investigated by various researchers include Sputtering[7,8], thermal evaporation [9], pulsed laser [1], Silar method [10], spray pyrolysis[11], sol -gel method[12],etc. In the present work ,Cu2Zn1-xCdxSnS4 thin films were prepared by spray pyrolysis technique, and their structural and optical properties were investigated.

II. EXPERIMENTAL

A Cu2Zn1_xCdXSnS4 (CZCTS) thin –films system (where x = 0 and 0.2) was prepared by chemical spray pyrolysis. The films deposited onto micro-glass slides were first cleaned with detergent water and then dipped in acetone. Spray solution were prepared by mixing 0.2 M aqueous solutions of CuCl2, ZnCl2, CdCl2, SnCl4,and thiourea [CS(NH2)2] at ratio of 2x:1-x: x: 1: 4 (Cu,Zn,Cd,Sn,S) using a magnetic stirrer. The automated spray solution was then transferred to the hot substrate kept at the normalized deposition temperature of 613K using filtered air as carrier gas at a flow rate normalized to approximately 3 ml/min. To prevent the substrate from excessively cooling, the prepared solution was sprayed on the substrate for 10 s with 15 s intervals. The films had a uniform thickness of (800) nm. the structural properties were determined by X-ray diffraction (XRD; Shimadzu) with CuKα radiation (λ = 1.5406 Å). Film morphology was analyzed by atomic force microscope (AFM)- type (CSPM).The optical absorption and transmission spectra were obtained using a UV-vis spectrophotometer (6800 JENWAY, Germany) within the wavelength range of 300 nm to 1100 nm.

III. RESULTS AND DISCUSSION

The structures of the Prepared CZCTS thin films were investigated by XRD. The XRD patterns in Figure 2 show the major diffraction peaks at 2θ= (28.59) and (28.4) for CZTS at x = 0 and for CZCTS at x = 0.2. The increase in cadmium (Cd) as shown by the shift in the main diffraction peak to a lower value of 2θ is attributed to the increase in lattice spacing of the longer Zn atom (1.71 A°) substation for smaller Cd atoms (1.53 A°) [4]. This result corresponds with that reported by Shannon et al [6]. Furthermore, an increase in the main peak intensity is observed in the presence of cadmium. A comparison with ASTM card JSPDS 26-0575 reveals that the CZTS (x = 0) thin film exhibits a crystal structure tetragonal type of kestrits phase with a preferred orientation (112) and other planes, i.e., (220) and (312). For 2θ= (28.59, 47.5, 56.1).. This result agrees with that reported by Pawar et al.[13] The CZCTS film at x=0.2 has a tetragonal phase.

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Secondary phase such as Cu2S (110) and ZnS (101) corresponding with card JSPDS 46-1195 and card JSPDS 36-1450 are observed in all samples. Kamoun et.al[14] observed the presence of CuS and Cu2S as secondary phase in spray deposited CZTS Film. The crystalline size (D) is determined from the main peak of 2θ= (28.59,28.4) and found to be equal to 40 and 43 nm (Table 1) based on the Scherer formula [15].

The AFM images of the films at x = 0 and 0.2 on glass are shown in Figure 3, The image shows the presence of homogenous grains throughout the film The grain size of these film is 88.5 and 94.6 nm for the two x values, respectively, The roughness (R) and root mean square vary from (1.85-1.96)nm and (2.25-2.33)nm respectively. The film roughness increases with increased grain size. This result agrees with that reported by Hossain et al. [5]

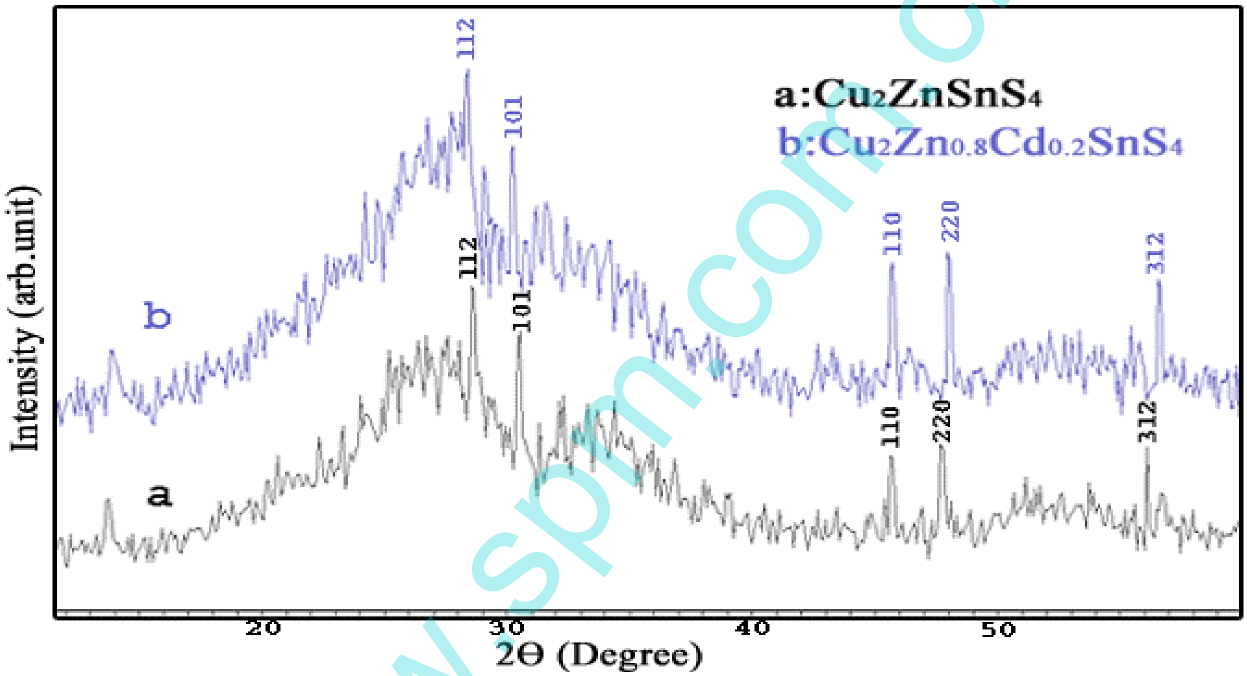

Fig.2: X-Ray diffraction patterns of $Cu_2Zn_{1-x}Cd_xSnS_4$ thin films(a) x=0, (b) x=0.2 .

Table.1
phases, planes and grain size of prepared films.

X	Grain size	2θ	hkl	Crystal system
0	40nm (28,59)	28.57	112	Tetragonal
		30.52	101	Cubic
		45.72	110	Hexagonal
		56.2	312	Tetragonal
		47.8	220	Tetragona
0.2	43nm (28.43)	28.43	112	Tetragonal
		30.49	101	Tetragonal
		45.7	110	Hexagonal
		47.77	220	Tetragonal
		55.9	312	Tetragonal

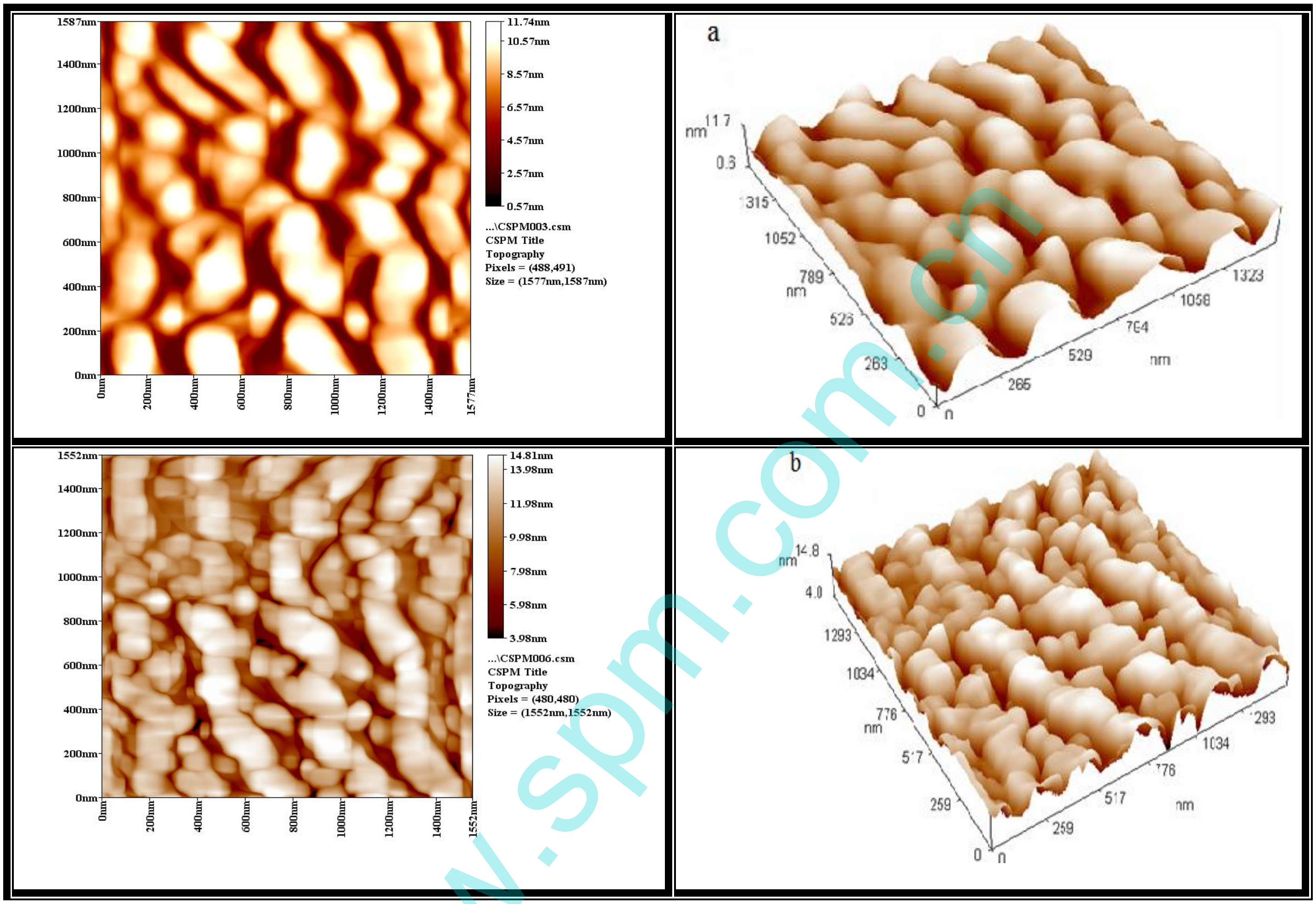

Fig. 3 the atomic force microscope (a) 2-D and 3-D Image for *x*=0 , (b) 2-D and 3-D Image for *x*=0.2

Figure (4) show the absorption coefficient (α) and energy gap (Eg) .The absorbance layers of CZCTS were measured from 300nm to 1100nm. Figure 4(a) shows the plot of α (cm-1) versus the wave length λ, which suggests that the two Film exhibits high absorption coefficient (> 104 cm-1). Thus a very thin layer of film (1-2μm) can absorb over 90% of photons over the spectrum , with higher photon energy in the bandgap. The optical properties of the CZTS layer can be improved with a substitution of Zn atoms by Cd atoms to give lower energy gap gap, because since ZnS has a direct optical band near 3.6 eV that gives a higher energy gap of CZTS. The optical band gaps of CZTS film and CZCTS are shown in Figure 4b. The absorption edge shifts to the NIR region with increased x.

The optical bandgap of CZCTS film is shown in Figure 4b from the plot of (αhv)2 as a function of photon energy hv according to the Tauc formula for direct bandgap semiconductors[16].

(αhv)2 = β(hv – Eg) ---------------------(1)

Where α is the absorption coefficient, β is a constant, Eg is the optical energy gap, v is the incident photon frequency, and h is Planck's constant . The obtained optical gap for CZTS is (1.7)eV which agrees with the CZTS bandgap value reported by Moholkar et al. [1]and 1.66 eV for CZCTS at x = 0.2. Eg decreases with increased cadmium content. This result corresponds with that of Altosaar et al. [2]

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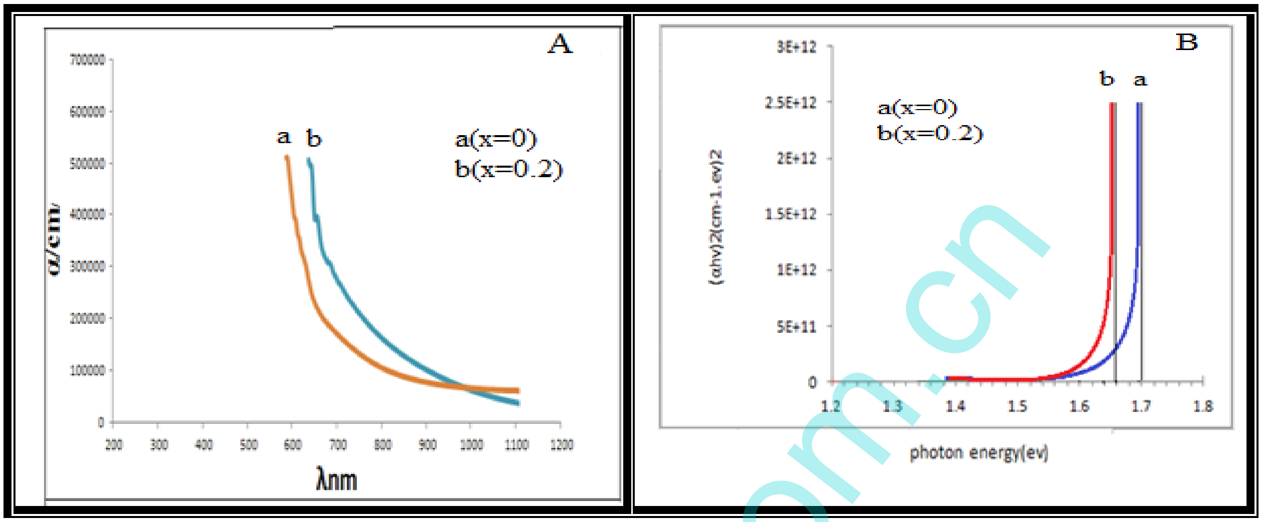

Fig 4. (A) The absorption coefficient (α) and (B)band gap (Eg) of prepared films at x=0 and x=0.2.

IV. CONCLUSIONS

CZCTS thin films are successfully deposited by spray pyrolysis technique . The effect of Cd content in the film on the structural and optical properties is investigated. XRD analysis indicates that the deposited films have nano crystalline kesterite structural, the crystalline sizes vary within the range of (40-43) nm with increased Cd element. The AFM images show homogenous grain films with grain sizes ranging from(88.5)nm to (94.6) nm The optical properties of the films exhibit a high optical coefficient (>104 cm-1) with a direct energy gap of (1.7) eV for CZTS and (1.66) eV for CZCTS films. The deposited films are contain secondary phase which is Zns and Cu2S. The deposited films contain a secondary phase that is ZnS and Cu2S. The prepared CZCTS film seems to possess structural and optical properties suit**able for absorber layers in efficient thin-film solar cells.**

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