Available online at https://www.irjst.com/
International Research Journal of Science and Technology
ISSN:2707-3955
DOI: https://doi.org/10.46378/irjst.2020.010211

The influence of Deposition Temperature on the Properties of Chemically Sprayed Nanostructured Cu_2CdSnS_4 Thin Films

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Paper Status

Received	:	January 2020
Accepted	:	March 2020
Published	:	March 2020

Abstract

In this study, Cu_2CdSnS_4 thin films were deposited on glass substrates at fixed concentrations: 0.02 M of ($CuCl_2.2H_2O$), 0.08 M of CS $(NH_2)_2$ and 0.01 M of both $SnCl_2.2H_2O$ and ($CdCl_2.2H_2O$) using Chemical Spray Pyrolysis (CSP) technique at different deposition temperatures (300, 350, 400 and 450) °C. The thickness of all samples were (300 ± 10) nm. X-ray diffraction patterns showed that all films have a tetragonal structure with a preferred orientation of (112). The maximum value of the crystallite size was 8.09 nm at 400 °C deposition temperature. Raman spectra analysis confirmed the purity of the film peaks located at (332-333). The FESEM micrographs showed that the nanostructures appeared in the form of cauliflower. The highest average grain size was 62.8 nm for the film deposited at 300 °C substrate temperature. The optical properties of all films were studied by recording the transmittance and absorbance in the wavelength range (400-900) nm. The results showed that absorption occurs in the visible and ultraviolet regions. Through the Tauc's equation, the optical energy gap was calculated for the allowed direct transition. Its value was in the range (1.59-1.40) eV. Therefore, these films are suitable for use in solar cell applications. Hall effect results showed that Cu_2CdSnS_4 thin films are p-type and the highest conductivity was 0.288 $(\Omega.cm)^{-1}$ at 400 ˚C corresponding to the maximum mobility value and the highest charge concentration.

Key Words
Chemical Spray Pyrolysis
Cu_2CdSnS_4
Deposition Temperature
Hall Effect
Nanostructures
Optical Properties
Structural Properties

Citation: Hiba J. Ahmed, Asaad A. Kamil, Ammar A. Habeeb, Nabeel A. Bakr. "The influence of Deposition Temperature on the Properties of Chemically Sprayed Nanostructured Cu_2CdSnS_4 Thin Films". International Research Journal of Science and Technology, 1 (2), 149-155, 2020.

1. Introduction

In recent years, there has been a great deal of interests in research field of chalcopyrite semiconductors due to their suitable band gaps and high optical absorption coefficient for potential application in thin film solar cells [1, 2]. Recently, higher power conversion efficiencies of solar cells based on Cu_2ZnSnS_4 and $Cu_2ZnSn(S,Se)_4$ as high as 8.4% and 10.1% have been reported [3,4].

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Because Cu_2CdSnS_4 structure is similar to Cu_2ZnSnS_4 and has a band gap of 1.37 eV and a large absorption coefficient 10^4 cm^{-1}, Cu_2CdSnS_4 is also considered as possible photovoltaic material [1,2]. Chemical spray pyrolysis technique has attracted many research groups to prepare different types of thin film materials because it is considered as a low-cost technique compared with other methods which usually require high-cost devices and complex instrumentation such as vacuum systems. Furthermore, it does not require high quality targets or substrates and can be easily scaled up for industrial applications [3]. In the current study, the structural, optical and electrical properties of Cu_2CdSnS_4 thin films deposited by chemical spray pyrolysis technique at different deposition temperatures are reported.

2. Experimental Details

Cu_2CdSnS_4 thin films were deposited on soda lime glass substrates by chemical spray pyrolysis. The substrates were cleaned ultrasonically in distilled water, acetone for (10 min) and then dried by air. The solution was prepared by mixing aqueous solutions of copper chloride dihydrate ($CuCl_2.2H_2O$) (0.08524 g in 25 ml), cobalt chloride dihydrate ($CdCl_2.2H_2O$) (0.0564 g in 25 ml), tin chloride dihydrate ($SnCl_2.2H_2O$) (0.0503 g in 25 ml) and thiourea ($SC(NH_2)_2$) (0.1522 g in 25 ml). The solutions were mixed by magnetic stirrer and left for few. The spray process was done using a homemade system at different substrate temperatures of (300, 350, 400 and 450) ˚C. The deposition conditions are described elsewhere [5]. The prepared films have good adhesive properties with a uniform thickness of (300±10) nm estimated by gravimetric method. The structural properties were investigated by using Grazing Incidence X-Ray Diffraction (GIXRD) (Ultima IV X-Ray diffractometer) with CuKα radiation (λ = 1.5406 Å) as the source. Topography of the surface of the deposited films was imaged using FESEM (MIRA3, TE-SCAN). Raman spectra were recorded at backscattering configuration using (Jobin-Yvon Horiba Labram800). The optical transmission and absorption spectra of the films were recorded by (Shimadzu, UV- 1800) in the wavelength range of (350–900) nm. Hall effect measurements were conducted by using (Ecopia HMS 3000).

3. Results and Discussion

The results of the X-ray diffraction test of Cu_2CdSnS_4 thin films prepared at different substrate temperatures (300, 350, 400 and 450) °C are shown in Figure 1 and Table 1. The results show that the patterns possess many peaks with a clear peak at (2θ≈28˚) corresponding to the direction (112). These results match well the data of ICDD card number (29-0537) which shows peak locations at (2θ=28.29˚, 47.12˚, 56.102˚, 68.366˚, 32.728˚, 69.229˚) [4,6]. The intensity of the peaks of these films increases with increasing the temperature of the substrate, and this indicates the increase in the crystallization and the reduction of crystal defects. Note that there are no peaks for secondary phases such as binary and high compounds (Cu_2S, SnS, Cu_2SnS_4, $CdSnO_3$). It can be also observed that the peak in the direction (112) is more prominent than its peers and this is due to the effect of deposition temperature on the growth in this direction [7]. The volume of the unit cell of all samples prepared was smaller than the standard volume (326.51 $Å^3$), where the unit cell suffered stress. The values of the lattice constant for the films are consistent with the values found in the standard card no. of the material which is (a= 5.487 Å and c= 10.84 Å). The estimated values of c/a of all samples are greater than that of the standard value (1.976) which indicates that the unit cell is elongated along the c-direction. The crystallite size of the samples was estimated using the well-known Scherrer's formula [8]:

$$D = \frac{0.9\lambda}{\beta\ cos\theta} \quad (1)$$

Where D is the crystallite size, β is the full width at half maximum (FWHM), λ is the X-ray wavelength of CuKα and θ is the Bragg's angle. The increase in the size of the crystals is due to the increase in temperature, which leads to an increase in the kinetic energy of the arranged atoms, which makes it easier for them to work in their correct locations in the crystal network. The highest crystallite size was 8.09 nm for the sample deposited at 400 °C. The low crystallite size is likely to be present in nanostructures [9]. The texture coefficient (Tc) was calculated using equation (2) describing the predominant trend of prepared films (112) as shown in Table 1 [10].

$$T_{c\,(hkl)} = \frac{I_{(hkl)}/I_{\circ(hkl)}}{N_r^{-1}\sum I_{(hkl)}/I_{\circ(hkl)}}$$

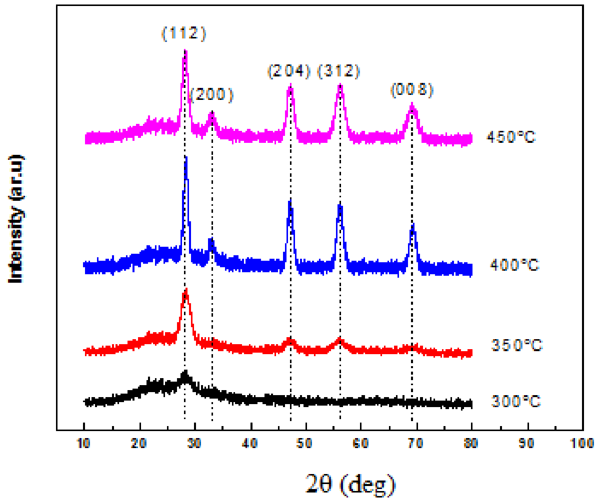

Figure 1. X-ray diffraction patterns of Cu_2CdSnS_4 thin films.

The obtained Raman spectra shown in Figure 2 confirm the formation of Cu_2CdSnS_4 with purified stannite phase of all prepared film samples. The recorded spectra for the samples shown in black color were analyzed using the origin pro.8.5 program, where several peaks were obtained (green color), one of which is the main peak (332-333) cm^{-1}, and the others are located at (328,250, 253, 283, 350 and 353) cm^{-1} [4,6] as shown in Table 2.

The results of Raman spectra shown are fully consistent with the results of X-ray diffraction, though; they often complement each other and strongly confirm that Cu_2CdSnS_4 films in the pure phase free from the secondary phases.

Table 1. X-ray diffraction results of the CCTS thin films.

Deposition Temperature (˚C)	300	350	400	450
hkl	112	112	112	112
2θ (deg.)	28.22	28.28	28.30	28.24
d_{hkl} (Å)	3.16	3.15	3.15	3.16
FWHM (deg.)	1.39	2.27	1.06	1.35
Lattice constant (a) (Å)	5.40	5.46	5.46	5.45
Lattice constant (c) (Å)	10.80	10.88	10.85	10.86
c/a	2.000	1.993	1.987	1.993
Unit Cell Volume ($Å^3$)	314.928	324.350	323.456	322.569
D (nm)	6.30	3.61	8.09	6.33
$T_{c(hkl)}$	1.12	1.33	1.22	1.20

Table 2. Results of Raman analysis.

Deposition Temperature (˚C)	Center of Peak (cm^{-1})	Width of Peak (cm^{-1})	Intensity (a.u.)
300	283	10.89	3.90
	333	16.05	60.01
350	328	8.10	7.17
	332	5.03	70.13
	353	8.81	2.91
400	250	4.39	2.84
	283	6.14	9.92
	333	5.00	99.88
	353	7.21	4.11
450	250	4.52	2.28
	283	9.77	8.02
	333	7.00	80.11
	353	5.80	2.02

The morphology of the prepared thin films was studied using FESEM, which depicts the surfaces in high magnification and high resolution (50KX). The images of Cu_2CdSnS_4 thin films prepared at different deposition temperatures are shown in Figure 3. It can be observed that the prepared Cu_2CdSnS_4 thin films have cauliflower-like forms with an irregular particle sizes and have some cracks and voids resulting from crystalline defects with secondary growth on the surface and this means the growth of a new layer before the completion of the previous layer [11,12]. The average grain size values of all samples are shown in Table 3.

Figure 4 shows the absorption coefficient as a function of the wavelength of the Cu_2CdSnS_4 thin films. The obtained results showed high values of the absorption coefficient ($\alpha > 10^4 cm^{-1}$) in the visible spectrum and ultraviolet, indicating a high probability of direct electronic transitions. The energy gap value of direct electronic transitions was calculated by plotting a graphical relationship of $(\alpha h\nu)^2$ versus photon energy ($h\upsilon$) and taking the best straight portion after the fundamental absorption edge to intersect the photon energy at ($(\alpha h\nu)^2=0$) as shown in Figure 5. The energy gap values for the Cu_2CdSnS_4 films was found to be in the range of (1.59-1.40) eV as shown in Table 4 which

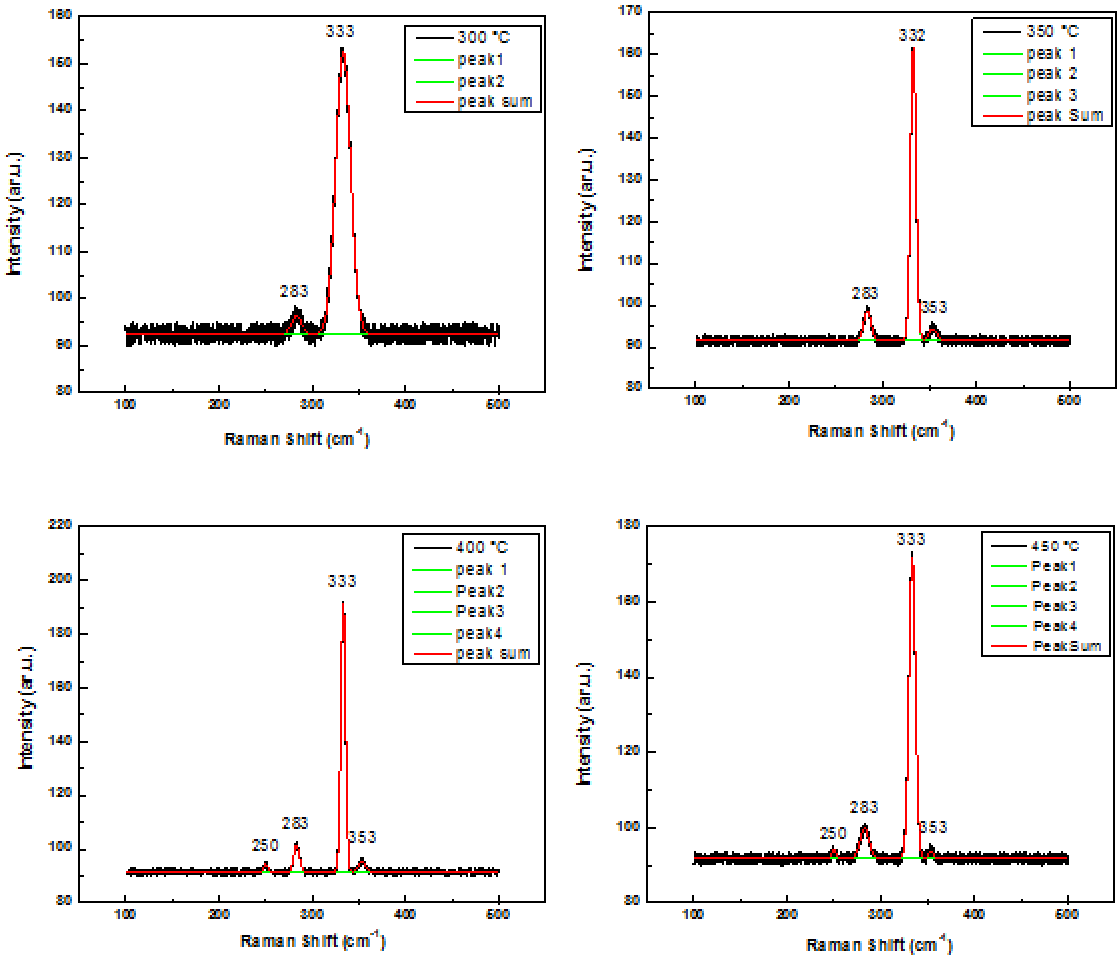

Figure 2. Raman spectra of Cu_2CdSnS_4 thin films under test.

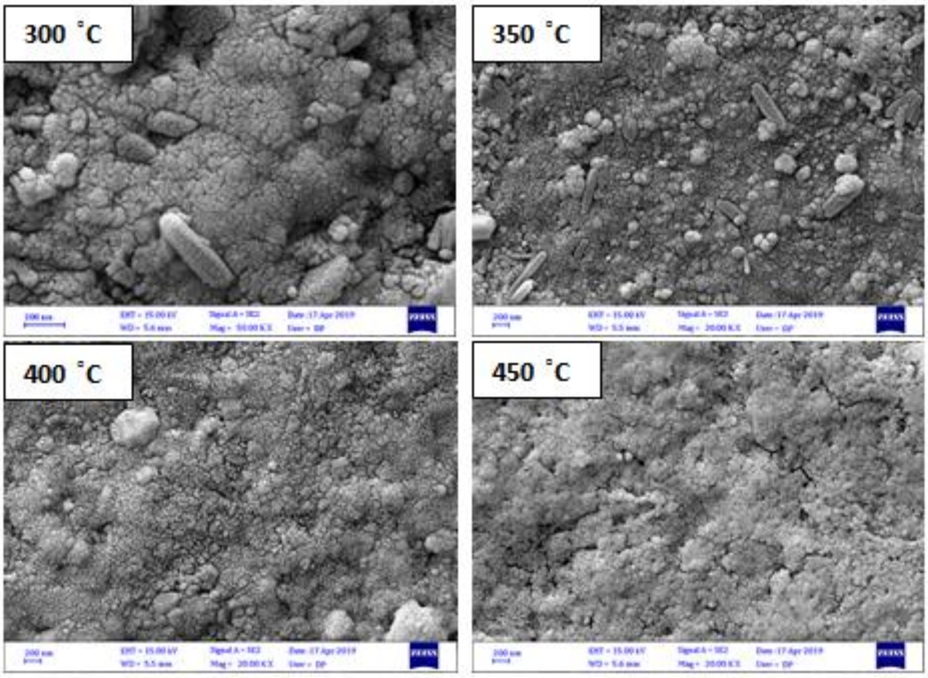

Figure 3. FESEM images of Cu_2CdSnS_4 thin films under test.

Table 3. Average grain size of Cu_2CdSnS_4 thin films.

Deposition Temperature (˚C)	Average Grain Size (nm)
300	62.8
350	61.1
400	52.9
450	54.2

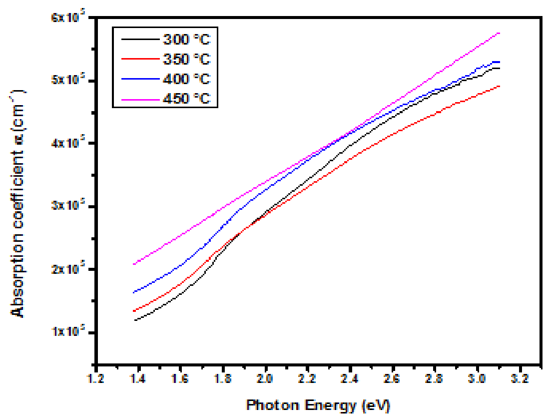

Figure 4. The relationship between the absorption coefficient and the photon energy of Cu_2CdSnS_4.

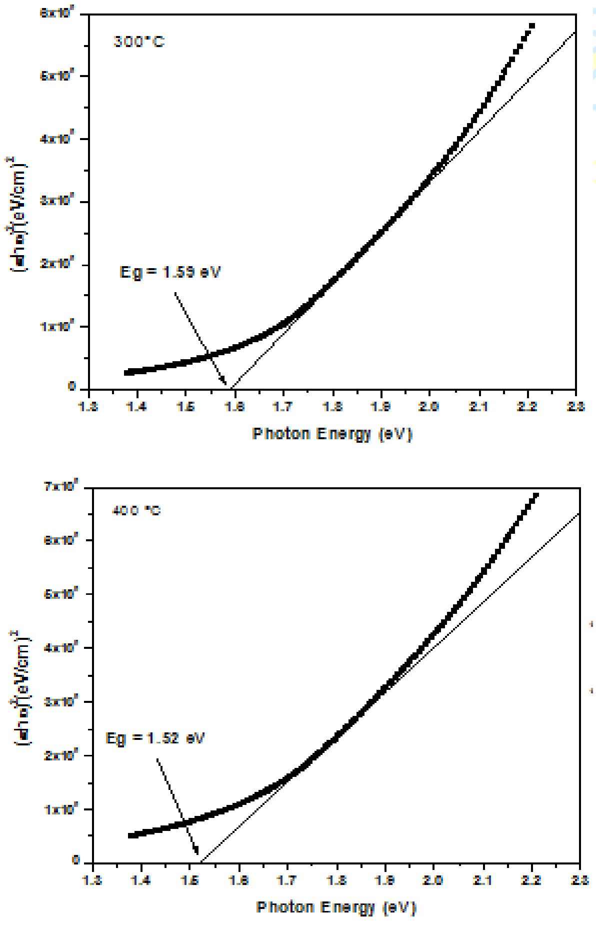

Figure 5a. The relation between $(\alpha h\nu)^2$ and (hν) for Cu_2CdSnS_4 thin films.

agrees well with results reported by previous studies [13-15]. These values are very close to those used for solar cell applications. The energy gap values depend on the crystalline structure in general and are affected by the increase in deposition temperature which is consistent with previous reports [11, 16-18].

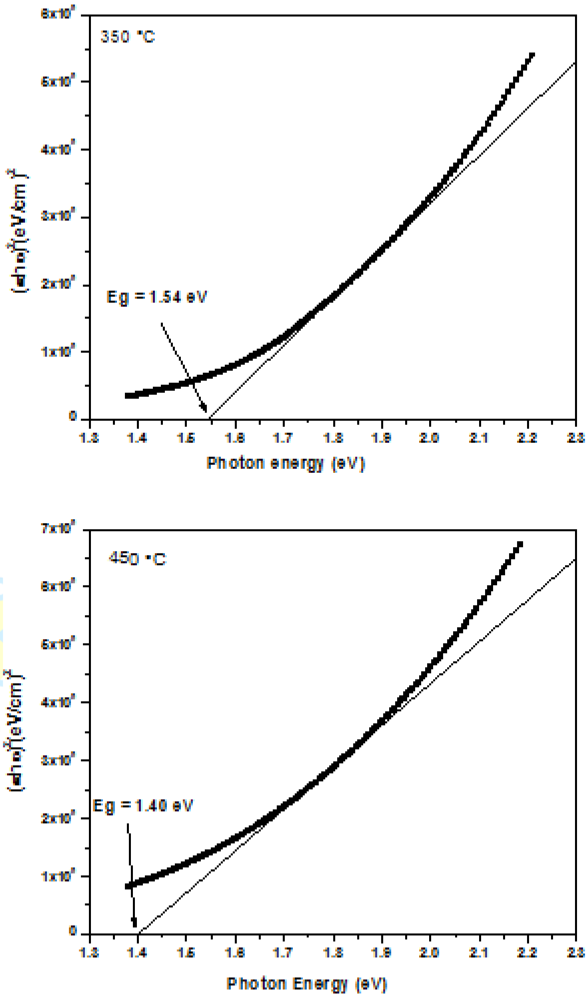

Figure 5b. The relation between $(\alpha h\nu)^2$ and (hν) for Cu_2CdSnS_4 thin films.

Table 4. Values of optical energy band gap of Cu_2CdSnS_4 thin films.

Substrate Temperature (°C)	E_g (eV)
300	1.59
350	1.54
400	1.52
450	1.49

Table 5 a and b shows the results of Hall Effect measurements. The highest electrical conductivity value was found to be 0.288 $(\Omega.cm)^{-1}$ for the film deposited at 400 °C and the highest mobility for charge carriers was 2.334 $(cm^2/V.s)$ for the same sample. The sign of Hall coefficient is positive which indicates that majority carriers are holes. Carrier concentration reaches its maximum value 7.71×10^{17} (cm^{-3}) for the sample deposited at 400 °C, which means that crystal growth has been completed [19].

Table 5. Results of Hall effect measurements.

Deposition Temperature (˚C)	R_H (cm^3/C)	n (cm^{-3})	μ $(cm^2/V.s)$	ρ (Ω.cm)	σ $(\Omega.cm)^{-1}$
300	22.533	2.77×10^{17}	0.323	69.71	0.0143
350	14.755	4.23×10^{17}	0.981	15.041	0.0664
400	8.095	7.71×10^{17}	2.334	3.468	0.2883
450	10.199	6.12×10^{17}	1.711	5.961	0.167

4. Conclusions

In this study, nanostructured Cu_2CdSnS_4 thin films were prepared by the chemical spray pyrolysis method at different substrate temperatures. From XRD and Raman analysis it was concluded that Cu_2CdSnS_4 films possess tetragonal structure having a stannite phase with a preferred orientation (112). All films are P-type. The substrate temperature 400 °C is distinguished by having the best structural, electrical and optical properties. The properties of the prepared films suggest that they can be a good candidate for absorbent layer in solar cells.

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