Effect of the Cd Concentration on the Characteristic Parameters of $Zn_{x-1}Cd_xS$ Thin Films Developed by Thermal Evaporation Method

Tariq J. Alwan
Physic Department , College of Education
Al Moustinsriay University

Abstract

The $Zn_{1-x}Cd_xS$ alloys were prepared in evacuated quartz tubes by the method of melt quenching. The $Zn_{1-x}Cd_xS$ thin films prepared by thermal evaporation method and at different value for x, (x= 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5).

X-Ray diffraction technique was used to study the structure of this films and the effect of x value on it . X-ray diffraction analysis confirmed that these films are polycrystalline structure nature having f.c.c , and lattice parameters are reported.

The most preferential orientation is along [111] direction for all deposited films. The lattice parameter, grain size, microstrain, dislocation density in the film are calculated and correlated with x.

D.C conductivity has been found that there are two stages of conductivity throughout the heating temperature range for polycrystalline films, The D.C conductivity of the as deposited films increases as x increased.

Optical energy gap of vacuum evaporated thin films in the $Zn_{1-x}Cd_xS$ system were calculated from absorptions spectra. It is found that the films exhibit allowed indirect transitions gap which decrease with increasing Cd content.

The relationship between the tail width and Cd composition in $Zn_{1-x}Cd_xS$ is calculated for each prepared films.

Introduction

Thin films of $Zn_{1-x}Cd_xS$ are known to have properties between those of CdS and ZnS. Because of the addition of ZnS, the $Zn_{1-x}Cd_xS$ band structure has a larger energy gap than CdS [1,2].

This makes the material much more attractive for the fabrication of solar cells [3-4]. $Zn_{1-x}Cd_xS$ thin films have been widely used as a wide band gap window material in heterojunction photovoltaic solar cells [3-4] and in photoconductive devices [5]. In solar cell systems, where CdS thin films have been proved to be useful, partial substitution of Zn for Cd increases the optical window of the heterojunction and also the diffusion potential [6-7]. Moreover, in heterojunction solar cells using $CuGaSe_2$, the use of $Zn_{1-x}Cd_xS$ instead of CdS can lead to an increase in photocurrent by providing a match in the electron affinities of the two materials. This hexagonal $Zn_{1-x}Cd_xS$ ternary compound is also potentially useful as a window material for the fabrication of p-n junctions without lattice mismatch in devices based on quaternary materials like $CuIn_xGa_{1-x}Se_2$ or $CuIn(S_xSe_{1-x})_2$[8].The Zn_xCd_{1-xS} thin films have been prepared by a variety of techniques, including spray pyrolysis [6,9], ion beam deposition [10], molecular beam epitaxial growth [11,12], and screen printing method [13,14].The evaporated films have been reported to have much higher conductivities [15].

In this paper, we study the structure, electronic and optical properties of $Zn_{1-x}Cd_xS$ thin film that prepared by using the thermal evaporation method and the effect of varying the concentrations of Cd in films.

Experimental

$Zn_{x-1}Cd_xS$ thin films were deposited on highly clean glass substrates in a vacuum better than (10^{-5} torr) by using thermal evaporation method. Pure ZnCdSe powder 99.99%, was used for deposition. The rate of deposition was (5Å/sec) and the source to substrate distance was kept at 12cm. The films are deposition at room temperature with different value for x=0.1, 0.2, 0.3, 0.4 and 0.5. The X-ray diffraction (XRD) patterns of the deposited films were recorded with the help x-ray diffractometer. Using CuKα radiation. The XRD patterns of all films were taken from (20^o to 60^o).

For the D.C conductivity measurement we have used D.C power supply PE-1540. and digital electomer Keithely 616 for current and voltage measurement.

UV/Visible spectrophotometer was used to obtain the absorptions and transmittance spectra, respectively. For the films that deposited on glasses substrates.

Absorptions spectrum was used to determine the optical energy gap. the value of $(\alpha h\upsilon)^n$ was plotted against the photon energy ($h\upsilon$) .The straight line portion is extrapolated to zero and the value which is obtained represented the optical energy gap.

Results and Discussion

1- Structure Properties

It is observed that all $Zn_{x-1}Cd_xS$ thin films are polycrystalline having f.c.c. zinc blend structure irrespective films. Fig.(1) represents the XRD patterns of six $Zn_{x-1}Cd_xS$ thin films that deposited at R.T with different value for x.

All films show the most preferred plane [111], these are observed which establishes the single phase cubic structure of the films [16].

From Fig.(1) the diffraction pattern exhibits the heights of peaks are increased with the increase of the concentration of Cd in the films. This mean that the crystallinlty of the films increased when the concentration of Cd increased [17].

The vacuum evaporated $Zn_{x-1}Cd_xS$ thin films cubic zincblende structure. It is confirmed by comparing the peak positions (2θ) of the XRD patterns of the films within standard X-ray powder diffraction data file. The lattice constant (a) for the cubic phase structure is determined by the relation [18]

$$a = d.\sqrt{h^2 + k^2 + l^2} \;\ldots\ldots\ldots\ldots\ldots\ldots 1$$

The lattice constant (a) then shows increasing tendency with increased the concentration of Cd, Fig. (2.a).

The change in lattice constant for the deposited thin film over the bulk clearly suggests that the film grains are strained and that may be owing to the change of nature and concentration of the native imperfections. The density of film is therefore expected to change in accordance with the change at lattice constant.[19]

It is observed that the XRD patterns of all $Zn_{x-1}Cd_xS$ thin films show a most preferred orientation along (111) plane. The [111] direction is the close-packing direction of the zincblende structure. The grain size of the deposited films is estimated using Scherer formula [18]

$$D = \frac{k\lambda}{\beta_{2\theta}\cos\theta} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where :

k is taken as 0.94,

λ: the wave length at X-ray used and $\beta_{2\theta}$ the full width at half maximum of

[111] peak of XRD pattern.

The grain size of the deposited films is decrease with increased concentration of Cd in films. As shown in table (1). The change of grain size with the Cd concentration , Is very prominent and this result agreement with Bedir et al [20]

The microstrain (ϵ) developed in the $Zn_{x-1}Cd_xS$ thin film is calculated from the relation [21]

$$\in = \frac{\beta_{2\theta}\cos\theta}{4} \;\ldots\ldots\ldots\ldots\ldots 3$$

A dislocation is an imperfection in a crystal associated with the misregistry of the lattice in one part of the crystal with that in another part. Unlike vacancies and interstitial atoms dislocations are not equilibrium imperfections. i.e thermodynamic considerations are insufficient to account for their existence in the observed densities. In fact the growth mechanism involving dislocation is a matter at importance. In the present study, the dislocation density is estimated from using the relation [19]

$$\rho = \frac{15 \in}{a D} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

for cubic thin films

It is observed that microstrain (ε) and dislocation density (ρ) exhibit increasing with x. (Fig. 2b and c), the increase of ε and ρ with x . may be due to decrease grain size.

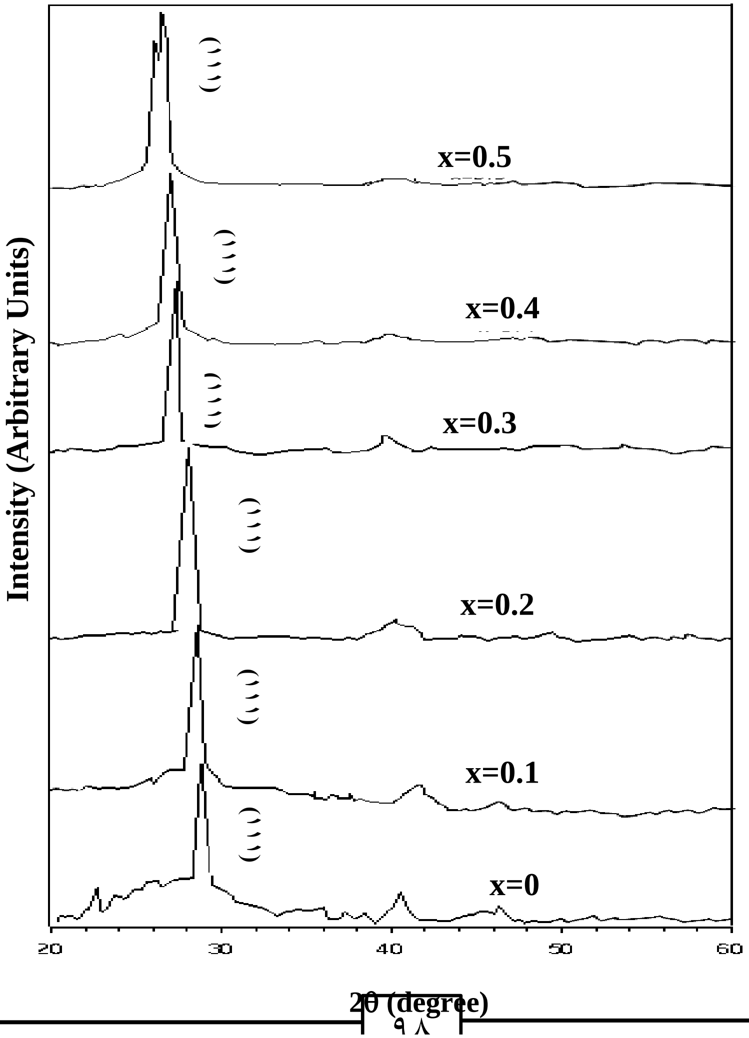

Figure (1): XRD traces for representative $Zn_{x-1}Cd_x$ S films

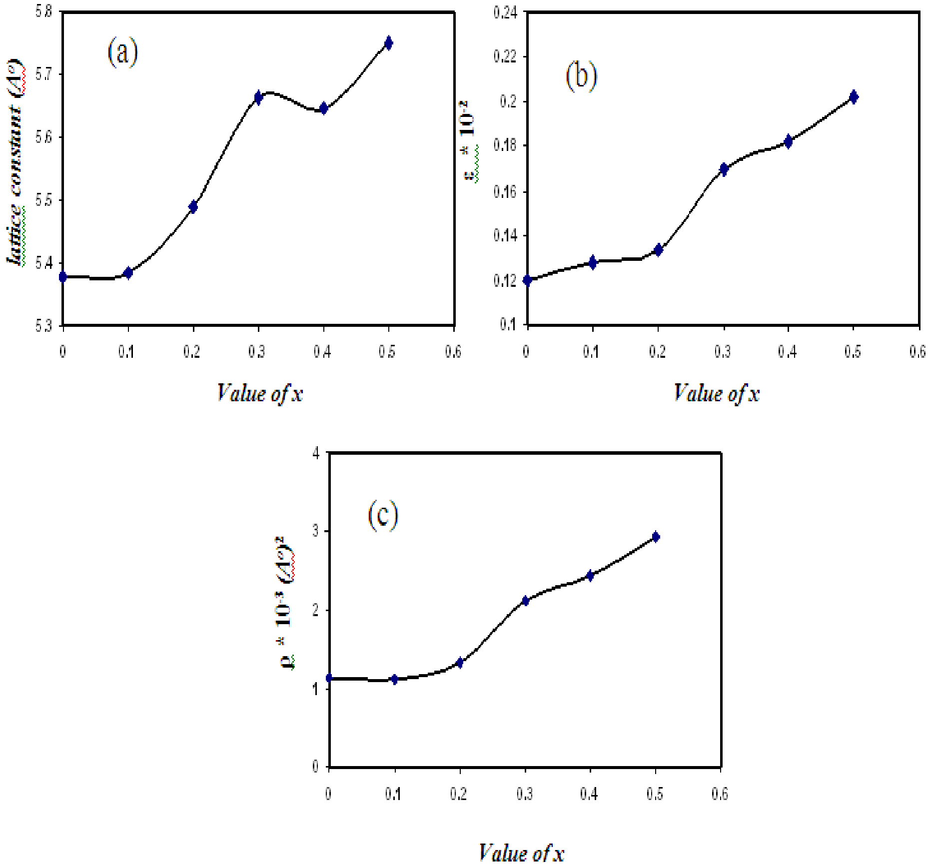

Figure (2): Variation of (a) Lattice constant, (b) Microstrain ε, and (c) Dislocation density ρ with x. in $Zn_{1-x}Cd_xSe$ films

2- D.C. Conductivity

The D.C. conductivity for $Zn_{x-1}Cd_xS$ films has been studied as function of $(10^3/T)$ for thin films of (x = 0.0, 0.1, 0.2, 0.3, 0.4, and 0.5)

From Fig.(3) we are found that there are two stages of conductivity throughout the heating temperature range . In this case the first activation energy (Ea_1) occurs at higher temperature within range (377-476) K and this activation energy is due to conduction of the carrier excited in to extended states beyond the mobility edge. While the second activation energy (Ea_2) occurs at low temperature within the range of (303-377) K and the conduction mechanism of this stage is due to carriers transport to localized states near the valence and conduction bands. These two conduction mechanism means that the D.C. conductivity is non-liner with temperature.

Fig.(3) shows the variation of (ln σ) versus. (1000/T) for $Zn_{x-1}Cd_xS$ thin films at T_s = room temperatures and (x=0.0, 0.1, 0.2, 0.3, 0.4 and 0.5), also table (2) show the effect of concentration of Cd in films on the activation energy (E_a). The behavior of $\sigma_{R.T}$ and Ea with (x) in general increasing , the value of $\sigma_{R.T}$ increase from ($3.99 \times 10^{-8}\ \Omega^{-1}.cm^{-1}$) at x = 0.0 to ($2.12 \times 10^{-5}\ \Omega^{-1}.cm^{-1}$) at x = 0.5, this can be attributed to the decreasing in Cd concentration in films this lead to increases in the number of vacancy in structure of films, this means that there is a increasing in the dangling bond, hence lead to increases in density of localize states.[22] and we can confirm that from tail width results as function to Cd concentration , see table (2).

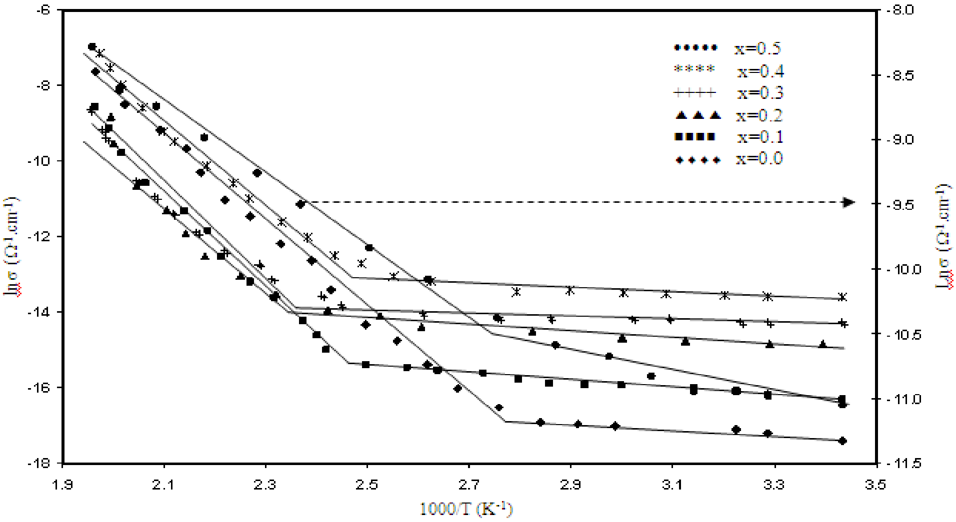

Figure (3): Variation of ln σ vs.1000/T for $Zn_{x-1}Cd_xS$ thin film deposited at room temperature for different value of x.

3- Optical Properties

The optical absorption of $Zn_{x-1}Cd_xS$ thin films was studied. The variation of optical absorption $(\alpha h\upsilon)^n$ with wavelength λ is shown in Fig. (4). All films show higher absorption on the shorter wavelength side. The nature of the transition (direct or indirect) is determined via the relation $\alpha = A(h\upsilon - Eg)^n$ where hν is the photon energy Eg is the band gap energy, and A and n are constants. For allowed direct transitions n = 1/2, for allowed indirect transitions n = 2. The plots of $(\alpha h\nu)^2$ versus hν are shown in Fig. (4) for $Zn_{x-1}Cd_xS$ films of various (x). Band gap energy Eg was determined by extrapolating the straight-line portion to the energy (αhν) . Table(2) shows variation in optical band gap energy decreased from 2.85 eV at x=0.0 to 1.75 eV at x=0.5. This is attributed to the crystallite size-dependant properties of the energy band gap [23-25].

And we see the change that happened in the structure of the films when increases the Cd concentration in films in section (1).

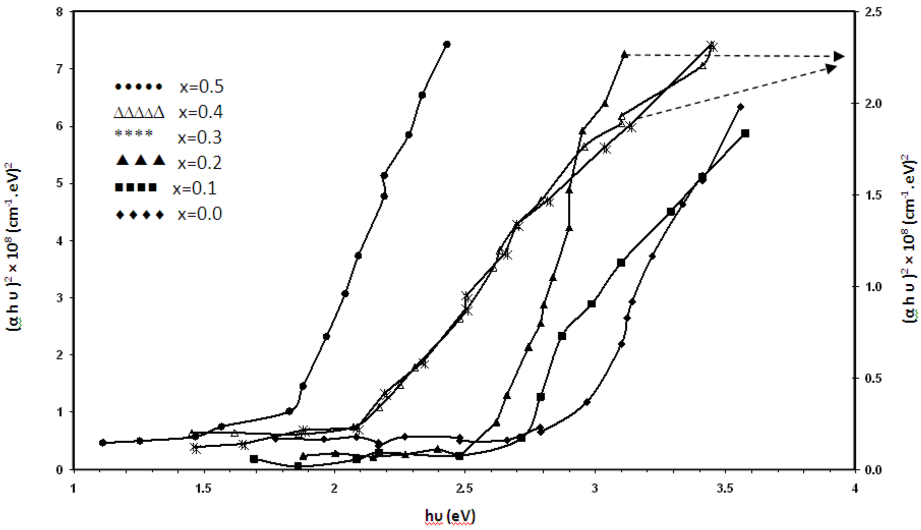

Figure (4) The variation of $(\alpha h\upsilon)^2$ with photo energy for $Zn_{x-1}Cd_xS$ thin films.

Table 1: Structural parameters of thermally evaporated $Zn_{x-1}Cd_xS$ thin films.

x	2Θ degree	d (Å)	[hkl]	a (Å)	D(Å)	$\varepsilon x10^{-2}$	$\rho x10^{-3}/A^{o2}$
0	28.73	3.103	111	5.379	298	0.120	1.129
0.1	28.67	3.103	111	5.384	281	0.1283	1.126
0.2	28.1	3.17	111	5.49	271	0.1333	1.342

0.3	27.5	3.27	111	5.663	212	0.1699	2.113
0.4	27.3	3.26	111	5.646	198	0.1822	2.437
0.5	26.8	3.32	111	5.75	179	0.2018	2.936

Table 2: Electrical and optical properties of thermally evaporated $Zn_{x-1}Cd_xS$ thin films.

x	**Ea1**	**Ea2**	**Eg**	**ΔE**
0.0	1.008	0.064	2.85	0.023
0.1	1.11	0.083	2.65	0.018
0.2	0.996	0.069	2.59	0.020
0.3	0.860	0.022	2.02	0.025
0.4	0.885	0.037	1.90	0.027
0.5	0.195	0.045	1.75	0.031

Conclusions

All thermally evaporated $Zn_{x-1}Cd_xS$ thin films at thickness (2500Å), deposited at R.T. with range (x=0.0 , 0.1, 0.2, 0.3, 0.4 and 0.5) are polycrystalline having f.c.c Zincblende type structure. Each films shows a preferred orientation along (111) plane .

The grain size of the deposited films has significant dependence on x. also all the other parameters that we calculated are changed with increase the concentration of Cd in the films.

This study showed that there are two transport mechanisms of charge carriers through the heating temperature range, the D.C conductivity increased with increasing the concentration of Cd in the films.

The optical energy gap for $Zn_{x-1}Cd_xS$ thin films have Indirect allowed transitions. The values of the optical energy gap were decreases as the Cd concentration increase

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تأثير تركيز الكادميوم على المعلمات المميزة لأغشية $Zn_{x-1}Cd_xS$ الرقيقة المحضرة بطريقة التبخير الحراري

طارق جعفر علوان

قسم الفيزياء، كلية التربية ، الجامعة المستنصرية

الخلاصة

تم تحضير سبائك $Zn_{1-x}Cd_xS$ في انبوبة من الكوارتز مفرغة من الهواء بطريقة التبريد المفاجئة. ثم حضرت اغشية $Zn_{1-x}Cd_xS$ الرقيقية بطريقة التبخير الحراري لقيم مختلفة لـ (x=0.0, 0.1, 0.2,0.3,0.4 and 0.5).

استخدمت تقنية حيود الأشعة السينية لدراسة تركيب تلك الاغشية وتأثير تغير قيمة (x) عليها. حيث اظهرت فحوصات الاشعة السينية ان جميع الأغشية المحضرة تمتلك تركيب متعدد التبلوري نوع متمركز الاوجه f.c.c., . بالإضافة الى معرفة قيمة ثابت الشبيكة. كل الاغشية المحضرة تمتلك توجه تفضيلي باتجاه [111].

اجري حساب الثوابت التركيبية مثل(ثابت الشبيكة، حجم البلورة، ، المطاوعة المايكروية، كثافة الانخلاعات) للاغشية المحضرة وحساب تأثير (x) عليها.

من قياسات التوصيلة المستمرة وجد انها تتكون من مرحلتين للتوصيل في الأغشية متعددة التبلور وقد وجد ان التوصيلية المستمر تزداد كدالة لتركيز الكادميوم في الأغشية.

تم حساب فجوة الطاقة البصرية للأغشية المحضرة بطريقة التبخير الحراري بالاعتماد على طيف الامتصاصية . وقد وجد ان تلك الأغشية لها فجوة طاقة غير مباشرة وان هذه الفجوه تقل بزيادة تركيز الكادميوم في تلك الأغشية.

العلاقة بين تركيز الكادميوم و عرض الذيول أيضا تم حسابها لكل الأغشية المحضرة