Kinetics of Growth and Structural Characterization of $Cd_{1-X}zn_xs$ Thin Films Synthesized By Cbd Method

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ABSTRACT

In this paper, we reported the study of $Cd_{1-x}Zn_xS$ thin film which have been deposited on glass substrates by Chemical Bath Deposition (CBD) technique by using Cadmium sulphate, Zinc sulphate, thiourea, Ammonia and EDTA. The thickness of $Cd_{0.5}Zn_{0.5}S$ thin films with different deposition times, pH, and temperature are also study and show increase with increasing times pH, and temperature. The optimum condition to prepared $Cd_{0.5}Zn_{0.5}S$ thin films were obtained in times 3h, temperature 80 ºC, and pH 10.

Structure and surface morphology of $Cd_{1-x}Zn_xS$ thin films were characterized by X-ray diffraction (XRD**),** Atomic Force microscope (AFM), and Scanning Electron Microscopy (SEM) Measurements. The XRD indicates that all the grown films show only one diffraction peak located at (2θ= 26.7˚) with hexagonal structure in predominant (002). The average grain size changes from 9.3nm to 4.48nm with the increase in zinc content (x = 0 to 0.65). It was found that as the zinc content increases, the peak intensity decreases and for ($x \geq 0.7$) the films have amorphous character. The values of lattice constant 'a' and ' c' have been observed to vary with composition from 5.75 nm to 4.68 nm and 6.66 nm to 6.62 nm, respectively, with the increase in zinc content (x = 0 - 0.65). The AFM studies showed that the smooth surface texture was observed in the deposited $Cd_{1-x}Zn_xS$ films with x= 0.3, the surface roughness of the $Cd_{1-x}Zn_xS$ thin films is about 2.66nm to 9.47nm and the root mean square (RMS) is about 3.41nm to 11.9nm with increase in zinc content x = 0.3 to 0.6. The SEM exhibits that grains in the film are distributed to cover the surface of the substrate completely, the grains become small in diameters with increasing Zn-contents.

Keywords: $Cd_{1-X}zn_xs$ Thin Films, Chemical Bath Deposition and Thin Film.

حركية النمو و خصائص التركيبية لاغشية $Cd_{1-x}Zn_xS$ المحضرة بطريقة الترسيب بالحمام الكيمياوي (CBD)

الخلاصة

في هذا البحث تم دراسة الأغشية الرقيقة $Cd_{1-x}Zn_xS$ المرسبة على قواعد زجاجية بأستخدام تقنية الترسيب بالحمام الكيميائي (CBD) من خلال أستخدم كبريتات الكادميوم و كبريتات

الخارصين والثايوريا والامونيا والعامل الكلابي EDTA. وجد السمك للاغشية الرقيقة $Cd_{0.5}Zn_{0.5}S$ المرسبة عند ازمان مختلفة وقيم مختلفة لدرجة الحامضية pH وعند درجات حرارة مختلفة يزداد بزيادة زمن الترسيب و دالة الحامضية و درجة الحرارة. الظروف المثلى لتحضير الاغشية الرقيقة $Cd_{0.5}Zn_{0.5}S$ تم الحصول عليها عندما يكون الزمن 3 ساعات و درجة حرارة 80ºC ودرجة الحامضية [pH=10] .

شخصت الخصائص التركيبية وهيئة السطح لاغشية الرقيقة $Cd_{1-x}Zn_xS$ بواسطة فحص حيود الاشعة السينية و مجهر القوة الذرية والمجهر الالكتروني الماسح . حيث تشير فحوصات الاشعة السينية الى ان جميع الأغشية تمتلك قمة واحدة عند الزاوية ($2\theta = 26.7^{\circ}$) مع تركيب سداسي يكون فيها المستوي (002) هو المستوي السائد على بقية المستويات , يتغير معدل الحجم الحبيبي من 4.48nmالى 9.3nm عند زيادة محتوى الخارصين **(** $x = 0 - 0.65$ **)** كما وجد ان زيادة محتوى الخارصين يقلل من شدة القمة وعند ($x \geq 0.7$) يصبح الغشاء عشوائي التركيب كذلك لوحظ ان قيم ثابت الشبيكة 'a' و'c' تتفاوت بين 5.75nm الى 4.68nm و 6.66 nm الى 6.62 nm , على التوالي وذلك يحدث عند زيادة محتوى الخارصين($x = 0 - 0.65$) . اظهرت دراسات مجهر القوة الذرية هيئة السطح ناعمة لاغشية $Cd_{1-x}Zn_xS$ عند قيمة ($x = 0.3$) ومعدل الخشونة للاغشية يتراوح بين 2.66nm الى 9.47nm ومربع متوسط الجذر يكون حوالي 3.41nm الى 11.9nm وذلك يحدث عند زيادة محتوى الخارصين ($x = 0.3 - 0.6$) . كما اظهرت قياسات المجهر الالكتروني الماسح ان الغشاء يمتلك حبيبات تنتشر على جميع اجزاء السطح ويصبح قطر هذه الحبيبات اصغر عند زيادة محتوى الخارصين .

INTRODUCTION

Over the last two decades, II-VI semiconductor thin films have attracted considerable attention from the research community because of their wide used in the fabrication of solar cells and other opto-electronic devices , with much interest shown in the use of Cadmium sulfide (CdS) as window layer of solar cells [1,2] . However, the absorption of the blue portion of the solar spectrum by CdS window results in a decrease in the current density of such solar cells [3-5] . For the high performance of solar cell device, it is imperative to use an appropriate window material. The growth of ternary semiconductor nano-microstructure thin film has been studied very extensively in recent years since these structures offer the prospect of high performance semiconductor laser diodes [6], photovoltaic and hotoconducting devices [7] . Ternary $Cd_{1-x}Zn_xS$ thin films often exhibit improved chemical, structural and optical properties and hence are potentially useful as a window layer in solar cells. It has been widely used as a wide band gap window material in hetero-junction photovoltaic solar cells and photoconductive devices. Keeping these aspects in view, more attention is being given in producing good quality $Cd_{1-x}Zn_xS$ thin films for comprehensive optical studies and their various applications [8].

EXPERIMENTAL DETAILS

The samples studied here were thin films of $Cd_{1-x}Zn_xS$ layers prepared by (CBD) on glass substrates. The substrates were washed with distilled water in order to remove the impurities and residuals from their surfaces, followed by rinsing in chromic acid for one day, (1gm of CrO_3 in 20 ml of distilled water) and finally wished again with distilled water. The aqueous solution of the deposition bath was prepared by the deposition addition of 30ml of 0.003M cadmium sulphate, 30ml of 0.003M Zinc sulphate, 30ml of

0.06 M Thioura,10ml Ammonia solution in 20ml distilled water and 30ml of EDTA of 1.2×10^{-4} M . The both compositions were used as shown in Table (1). The glass substrate is immersed in the solution vertically. After deposition of the films, substrates were taken out and thoroughly washed with in doubly distilled water and then dried in air. Thickness measurements were made by optical method, using He-Ne laser λ=0.632μm. Structural characteristic of the films were determined by X– ray diffraction system (Philips – PW1840) at room temperature with CuK_α radiation and wavelength λ = 1.5406Å. AFM type a scanning probe microscopy (CSPM-5000) instrument and SEM type VEGA TE SCAN, with an accelerating voltage of 30kV and magnification of 10000 x .

Table (1) Experimental on different bath compositions.

Material	*Molarities*	*Volume (ml)*
$Cd(SO_4).2H_2O$	**0.003**	**27, 24, 21, 18 , 15, 12 , 9 , 6, 3**
$ZnSO_4.7H_2O$	**0.003**	**3, 6 , 9 , 12, 15 , 18, 21, 24, 27**
$CS(NH_2)_2$	**0.06**	**30**
NH_3OH	**2.3**	**20**
EDTA	**1.2×10^{-4}**	**30**

RESULTS AND DISCUSSION

Optimization condition for deposition $Cd_{1-x}Zn_xS$ thin films

Cadmium Zinc Sulfide $Cd_{1-x}Zn_xS$ have properties in between CdS and ZnS, Because the solubility products of CdS (Ksp = 10^{-28}) and ZnS (Ksp =$10^{-23.8}$) are different by several orders of magnitude, the complexion agent is essential for codeposition. The influence of growth condition on the properties of $Cd_{1-x}Zn_xS$ was investigated to understand the deposition process and thus to improve the characteristics of the films. Therefore is used $Cd_{0.5}Zn_{0.5}S$ to deposition for optimization condition for deposition $Cd_{0.5}Zn_{0.5}S$ thin films.

Kinetics of Growth.

pH Effect for $Cd_{0.5}Zn_{0.5}$ S Thin Film

Figure (1) shows the dependence of deposition $Cd_{0.5}Zn_{0.5}S$ film thickness on different (pH) with temperature (80ºC) and time 3h. The film thickness is small at pH (8), the film thickness increases with increasing pH at (10) and subsequently decreases at higher pH (11). At low (pH) there is insufficient NH_3 to bind the Cd^{2+} and $Zn2^{+}$ into their complexes. This leads to an excess of Cd^{2+}, Zn^{2+} and S^{2-} in deposition bath and favors homogenous nucleation of $Cd_{0.5}Zn_{0.5}S$ colloids in solution with little film adhesion. At (NH_3) in the pH (10) , there is optimum NH_3 needed to Cd^{2+} and Zn^{2+} into their complex. At concentration higher than (10), the film thickness decreases. This is due to the over stabilization of the complexes at very high ammonia concentration which subsequently reduce the growth rate [9,10]. Therefore the best pH used to deposition $Cd_{0.5}Zn_{0.5}S$ films is (10).

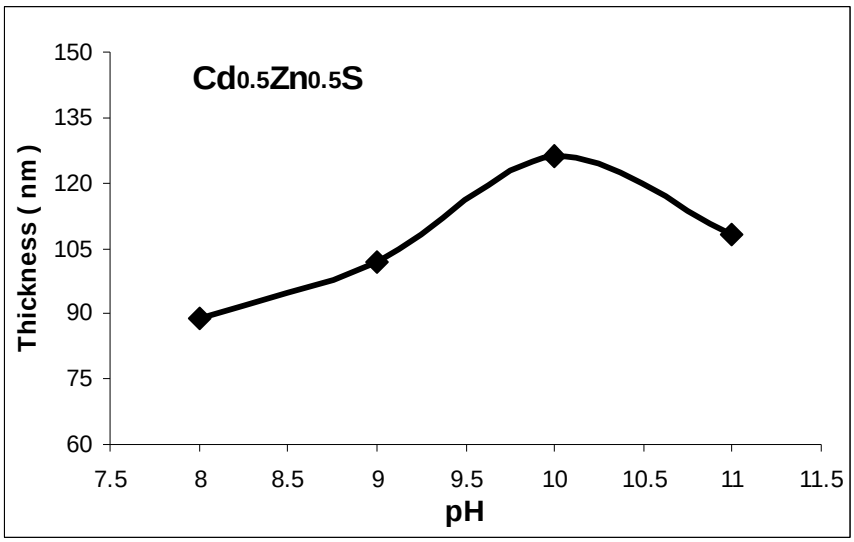


Figure (1) Influence of pH on $Cd_{0.5}Zn_{0.5}S$ film thickness.

Deposition Time Effect

The effect of deposition time on the thickness is very obvious in Figure (2), which explains the film thickness of $Cd_{0.5}Zn_{0.5}S$ film with different deposition times at temperature (80ºC) and pH (10). It is observed that the thickness of the film increases linearly with time and attains the maximum thickness after 3h. It is shown in the Figure that at longer deposition time (4h) there is no significant growth in film thickness. This is due to the fact that at longer deposition time the reaction in the bath is completed and thereafter, there is absence of free ions. Therefore the best time used to deposition $Cd_{0.5}Zn_{0.5}S$ films is (3h).

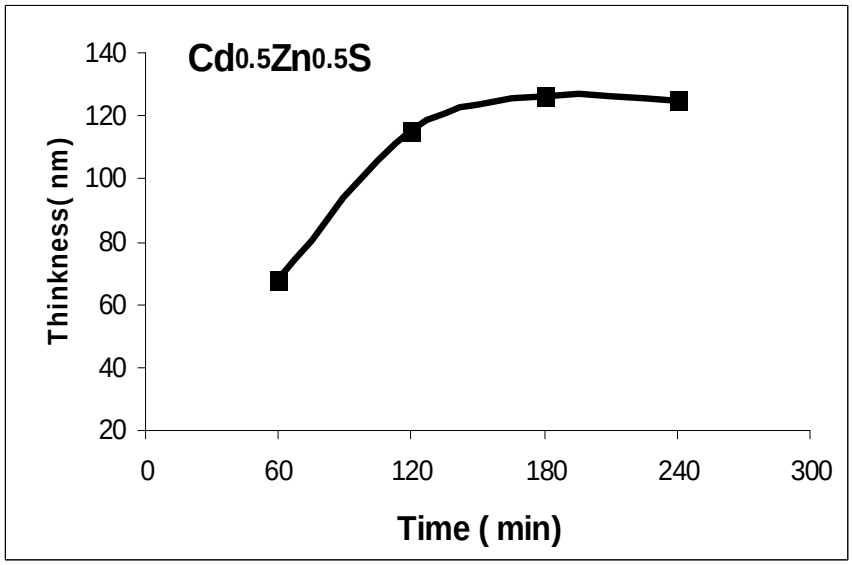


Figure (2) Thickness of $Cd_{0.5}Zn_{0.5}S$ thin film as a function of deposition time.

Temperature Effect

Figure (3) shows the film thickness of $Cd_{0.5}Zn_{0.5}S$ films at different temperatures. Throughout the figure it can be observe various temperatures from 60ºC to 90ºC were used in the depositing. The figure shows an increase in film thickness as temperature increases from 60ºC to 80ºC and drops at 90ºC, where the heating of the solution helps the decomposition of the reactants and produces the ions which are very necessary for film formation .The rise in the film thickness may be due to the increases in the hydrolysis of SC $(NH2)_2$ as the temperature increases [11]. Also the kinetic energy of the ions in solution is higher at higher temperature, which brings about increased interaction between them and subsequent deposition at volume nucleation centers of the substrate [12]. The observed decrease in film thickness at temperature above (80ºC) could be due to the decrease in ammonia concentration due to high evaporation rate at very high temperature. Therefore the best temperature used to deposition $Cd_{0.5}Zn_{0.5}S$ films is (80ºC).

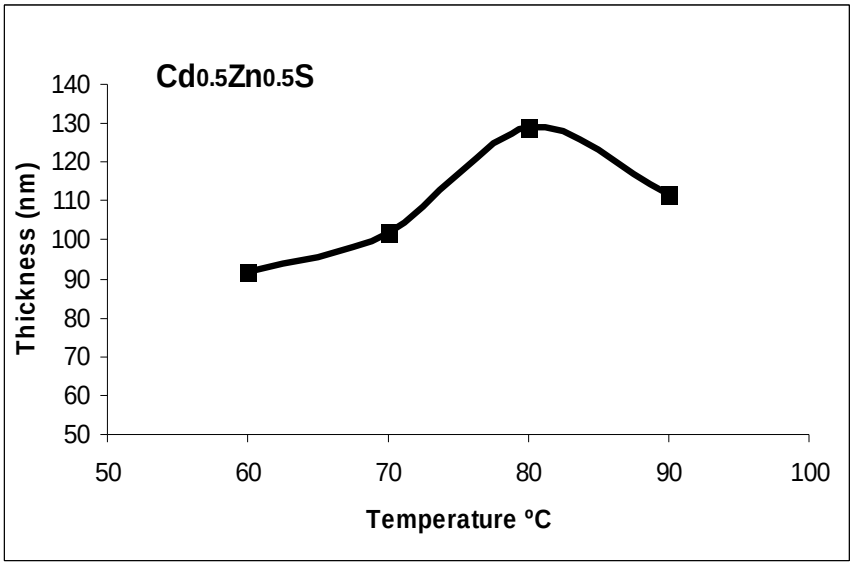


Figure (3) $Cd_{0.5}Zn_{0.5}S$ film thickness dependence on bath temperature.

Structural Properties

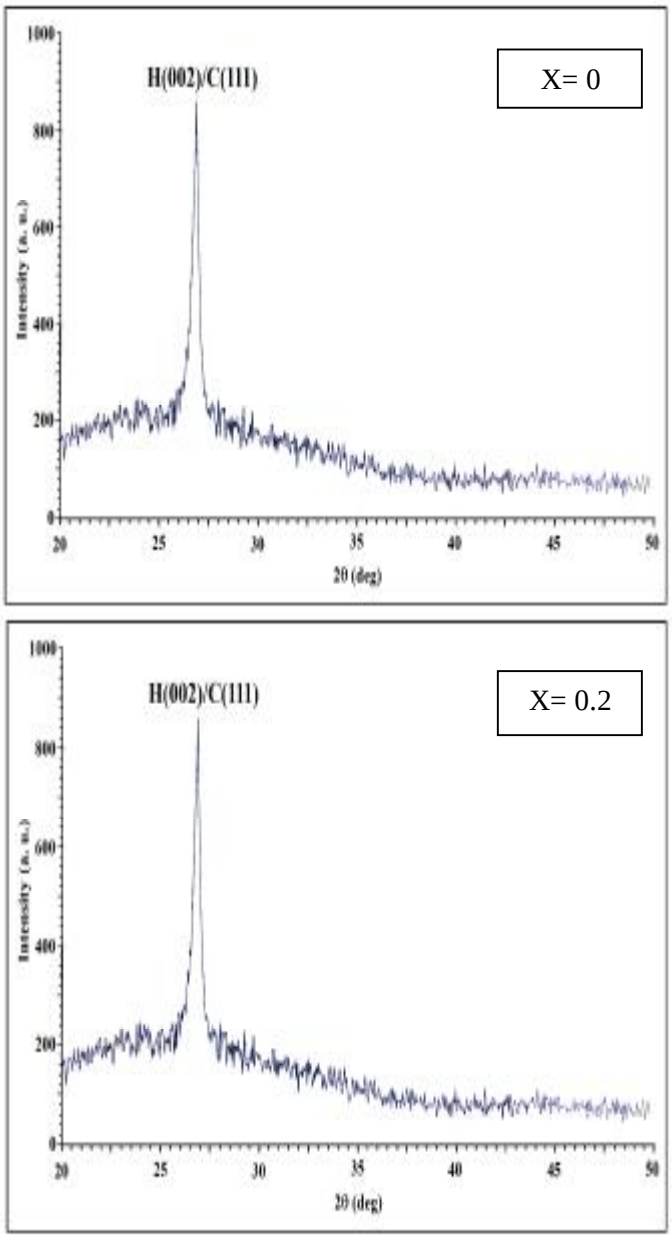
XRD Studied

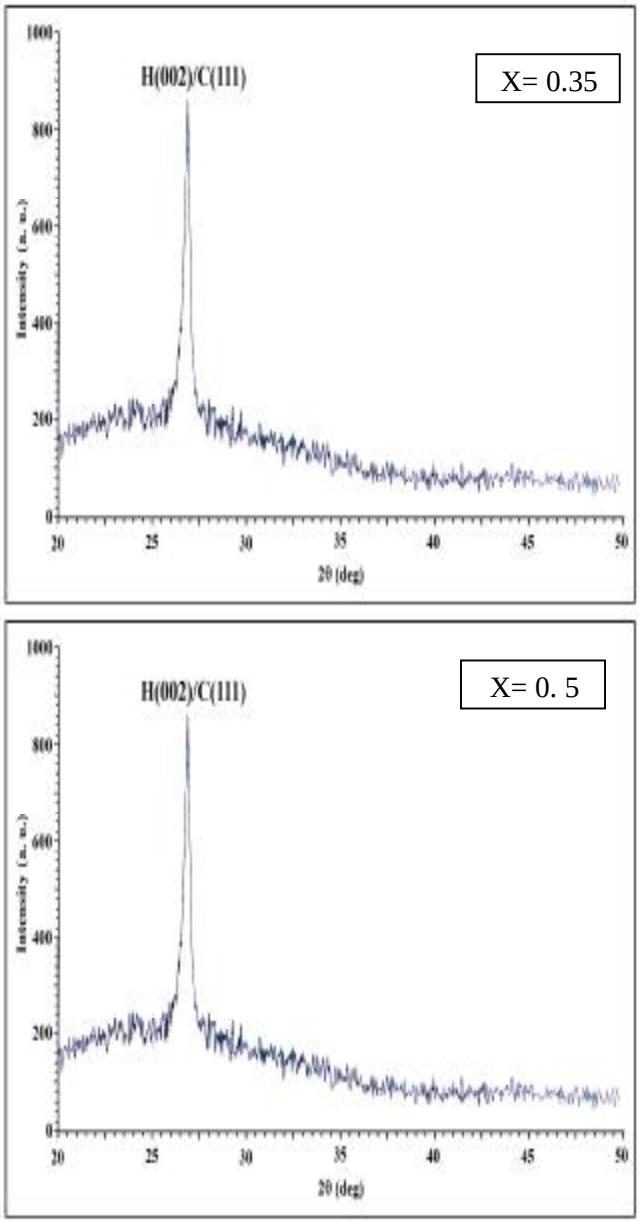
The structural identification of $Cd_{1-x}Zn_xS$ films was carried out with X-ray diffraction in the range of angle 2θ between 20^0 and 50^0. The grain size of $Cd_{1-x}Zn_xS$ film was determined by using Scherrer formula:

$$G.S=K\lambda/\beta\cos(\theta) \quad \text{.....(1)}$$

Where K is a constant taken to be 0.94, λ is the wavelength of X-ray used which is CuK_α radiation, β is the Full – width at half maximum (FWHW) of the diffraction peak corresponding to a particular crystal plane.

Figure (4) shows the X-ray diffraction for $Cd_{1-x}Zn_xS$ thin films on glass substrates at bath temperature ($80\,^0C$) for different Zinc content (x=0, 0.2, 0.35, 0.5, 0.65, 0.7) after annealed at 300ºC for 1h.





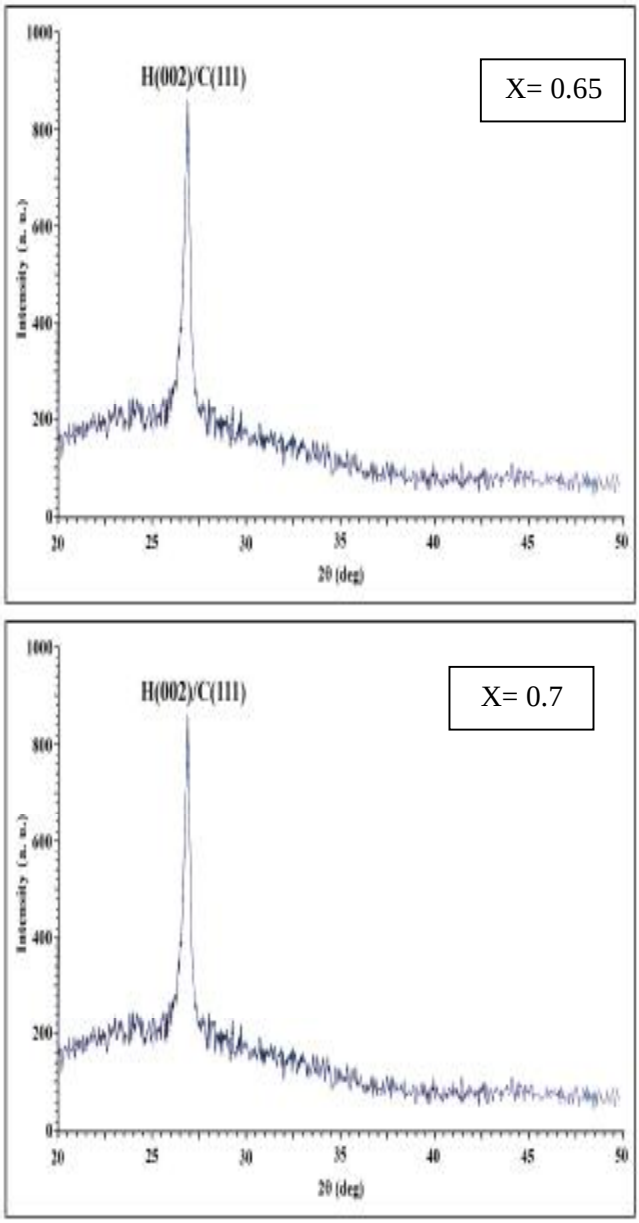


Figure (4) shows the X-ray diffraction for $Cd_{1-x}Zn_xS$ thin films for different Zn- content (x = 0, 0.2, 0.35, 0.5, 0.65 ,0.7) after annealed at 300ºC for 1h.

The X-ray diffraction data revealed that the crystallinity of the films depended strongly on the Zn-content in the layers. For all the Cd1-xZnxS films have exagonal structure as confirmed by standard ASTM data, which is consistent with another reports [13, 14], only one diffraction peak located around ($2\theta=26.7^{o}$). The angle position of the (002) peak moves toward greater values of angle with increasing Zn-content, which indicates that Cd^{2+} ions are successfully substituted by Zn^{2+} in the

CdS lattice [15]. Increases Zn-content gives rise to rapidly decrease in the peak intensity and it was disappeared when the Zn atomic (x) ≥ 0.7, this indicates that the degree of crystalinity decreases with increasing Zn-content in the film.

The lattice constant (a), (c) to the H(002)/C(111) plane as a preferred orientation for the CdS thin film and (002) plane as a preferred orientation for the $Cd_{1-x}Zn_xS$ thin films for different Zn-content (x = 0, 0.2 , 0.35 , 0.5 , 0.65) with the ASTM values have been listed in Table (2). Figure (5) shows the grain size decreases with increasing Zn-content.

Table (2) XRD parameters of ASTM and prepared $Cd_{1-x}Zn_xS$ thin films.

X	**2 deg)**	**d** XRD **(Å)**	**d** ASTM **(Å)**	**a** XRD **(Å)**	**a** ASTM **(Å)**	**C** XRD **(Å)**	**C** ASTM **(Å)**	**structure**	**G.S** (nm)
0	26.818	3.32	3.36	5.753	5.818			Cubic / Hexagonal	9. 33
0.2	26.739	3.331	3.34	4.71	4.112	6.66	6.68	Hexagonal	8.13
0.35	26.761	3.328	3.34	4.706	4.112	6.65	6.68	Hexagonal	7.10
0.5	26.790	3.325	3.31	4.702	4.069	6.65	6.62	Hexagonal	5.69
0.65	26.619	3.312	3.31	4.683	4.069	6.62	6.62	Hexagonal	4.48

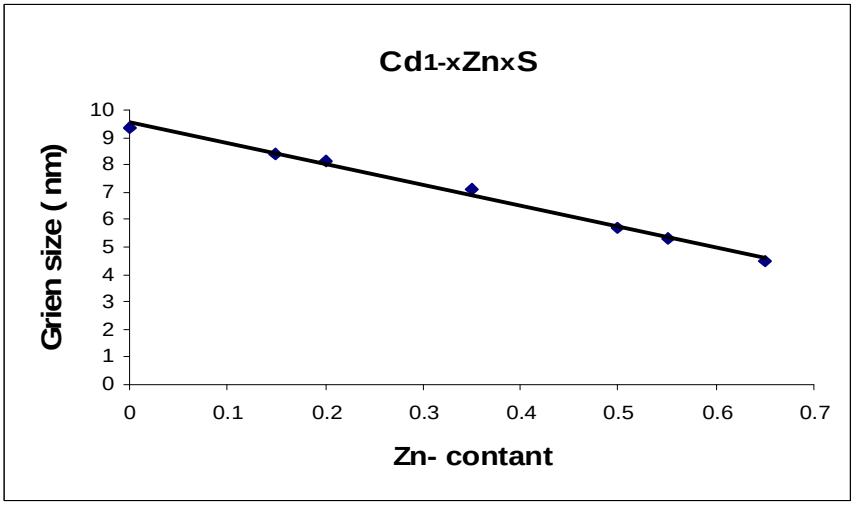


Figure (5) shows the variation of grain size versus Zn- content.

Atomic force microscopes (AFM) Analysis

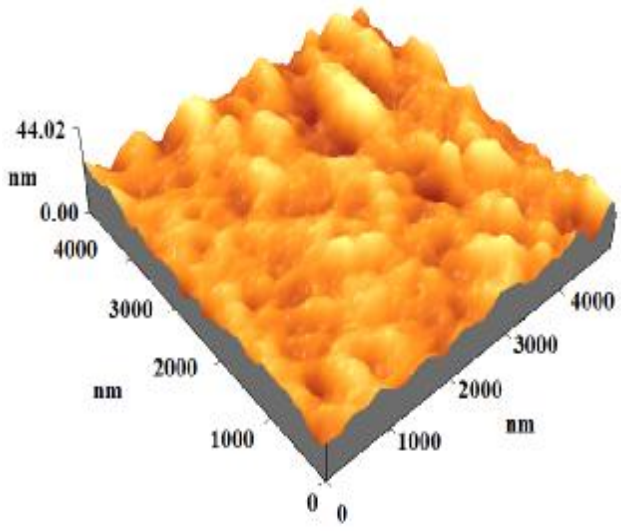
The surface morphology of $Cd_{1-x}Zn_xS$ thin films was analyzed using atomic force microscope, which indicated that Zn- content in the layers had a significant influence on the morphology. Figure (6 a ,b, c) shows the typical three - dimensional AFM image of $Cd_{1-x}Zn_xS$ films deposited at temperature 80°C , pH =10 and time 3h, after annealed at 300°C for 1h . The smooth surface texture was observed in the deposited $Cd_{1-x}Zn_xS$ films with (x = 0.3) , spherical shaped grains. The substrate surface is well covered with grains that are uniformly and regularly distributed over the surface

(Figure 6a). The AFM images of the films prepared using (x = 0.5 , 0.6) , where the size of the grains was rather different from each other indicating irregular growth rate of the grains.

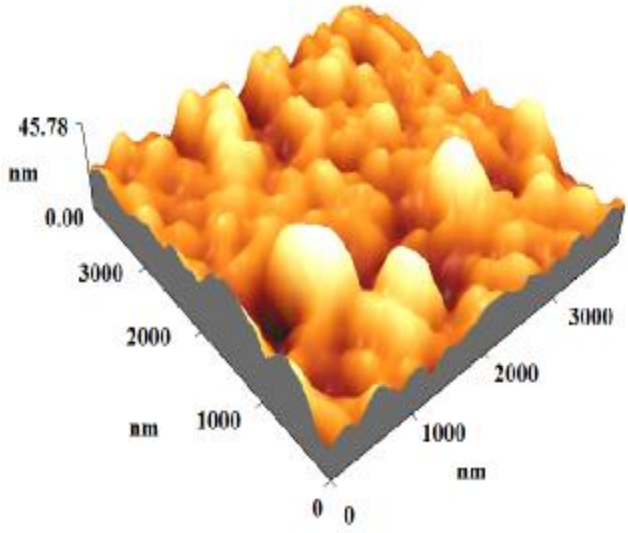
The root mean square (RMS) and the surface roughness average values were measured using atomic force microscopy technique. The root mean square and the roughness average values increase with Zn- content increase, and are listed in Table (3). The results show three different Zn -concentrated $Cd_{1-x}Zn_xS$ thin films exhibit different surface texture and the results indicate that roughness depends on the Zn-content and are found to increase with increasing x value .

Table (3) Variation of surface roughness with Zn- content for the $Cd_{1-x}Zn_xS$ films.

Zn- content (x)	The root mean square (RMS) (nm)	roughness average (nm)
0.3	**3.41**	**2.66**
0.5	**6.49**	**4.76**
0.6	**11.9**	**9.47**



(A)



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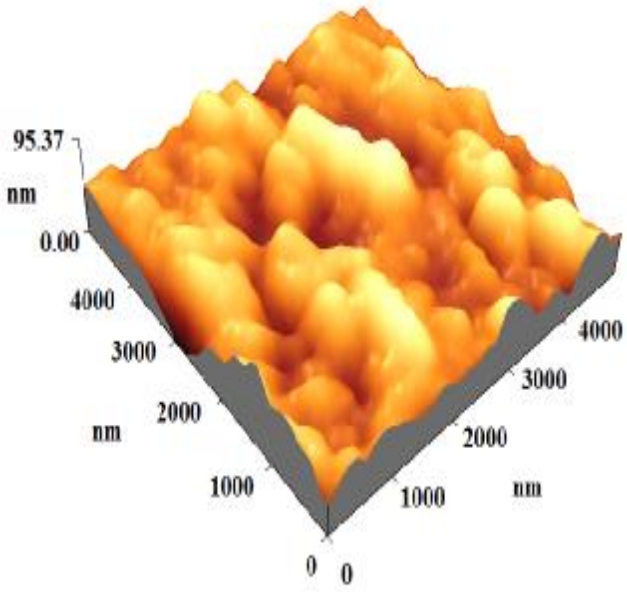


(C)

Figure (6) shows the AFM images of $Cd_{1-x}Zn_xS$ thin film with (a) X=0.3, (b) x=0.5, (c) x=0.6.

SEM Studied

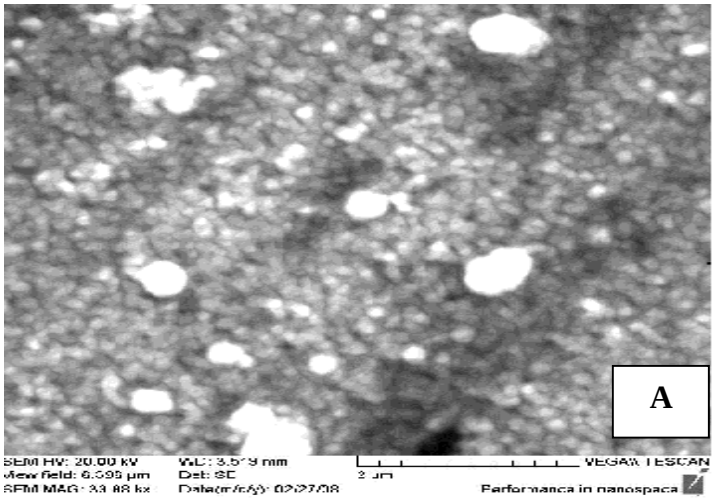
Figure (7 a, b, c) shows the scanning electron microscopy (SEM) for the films deposited at various Zn- content (x = 0.15 , 0.35 , 0.55) on a glass substrate by using (CBD) technique after annealed at 300ºC for 1h . The morphologies are different in these thin films. Considering first the film deposited at lower Zn-content (x = 0.15) the film exhibits grains distribution throughout the substrate and have surface consisting of wider grains as shown in Figure (7 a). With increasing Zn-contents at (x = 0.35) the films that have grains which are distributed to cover the surface of the substrate completely. The grains become small in diameter as shown in figure (7 b). With increasing Zn-contents at (x = 0.55), (Figure 7 c) smooth and more uniform films will be obtained as Zn - content increases. It is observed that the grain size decreases with increase in Zn - content.

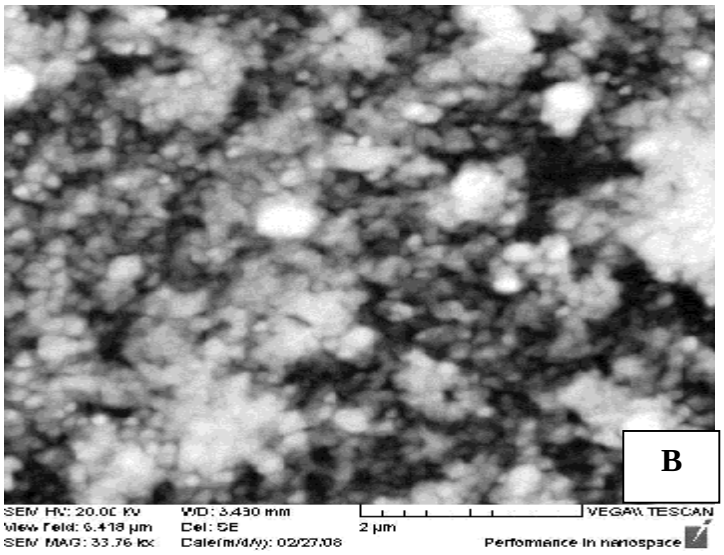
From the SEM images the grain size values of the $Cd_{1-x}Zn_xS$ thin films deposited by (CBD) technique are found to be in the range of (31-22) nm corresponding to the Zn-concentrations (x =0.15, 0.35, 0.55) respectively.

These values are larger than those with that estimated from XRD results as shown in Table (4).

Table (4) comparison between the grain size estimated from (XRD) and (SEM) analysis.

Zn-concentrations	Grain size estimated from (XRD) (nm)	Grain size estimated from (SEM) images (nm)
0.15	**8.40**	**31**
0.35	**7.10**	**26**
0.55	**5.33**	**22**





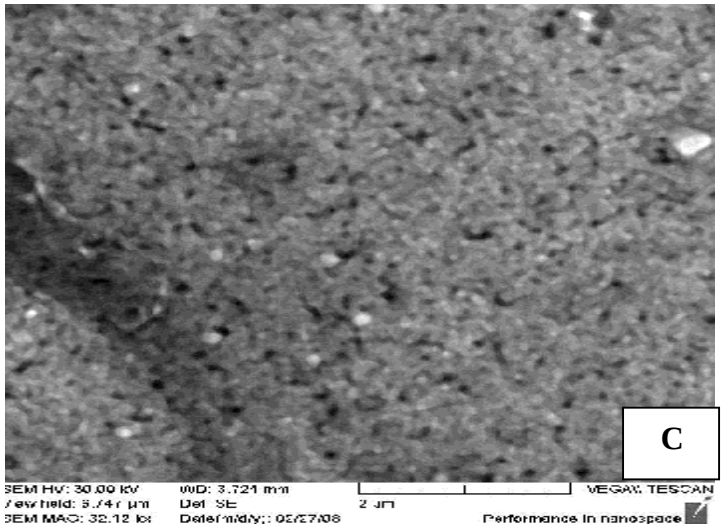


Figure (7 a, b, c) SEM image of $Cd_{1-x}Zn_xS$ thin films.

CONCLUSIONS

The main conclusions can be summarized as follows for $Cd_{1-x}Zn_xS$ thin films at different value Zn were prepared by Chemical Bath Deposition (CBD) method.

1- The thickness of $Cd_{0.5}Zn_{0.5}S$ thin films with different deposition times, pH and temperature increases with increasing times, pH and temperature.

2- The results of XRD show the $Cd_{1-x}Zn_xS$ thin films have been prepared by (CBD) at temperature 80^oC, pH=10 and t=3h with different Zn-concentrations,(x = 0, 0.2, 0.35, 0.5, 0.65) the films exhibited cubic/ hexagonal structure with a strong C(111)/H(002) orientation for (CdS) and hexagonal structure with a strong (002) orientation for the other concentrations (x = 0.2- 0.65) , the grain size, lattice constant (a,c) decreases with increasing Zn-contents.

3- The structure of $Cd_{1-x}Zn_xS$ thin films became amorphous with increasing Zn – concentration.

4- The results of AFM for the $Cd_{1-x}Zn_xS$ thin films, the smooth surface texture was observed with lower Zn– concentration and the root mean square and the roughness average values increases with Zn-content increase.

5- The results of SEM for the $Cd_{1-x}Zn_xS$ thin films, smooth and more uniform films will be obtained as Zn– content increase. It is observed that the grain size decreases with increase Zn-content.

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