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Indium doping effects on growth and preparation of spray pyrolysis deposited $Cd_{0.6}Zn_{0.4}S$ thin films

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ABSTRACT

Pure and Indium doped in Cadmium Zinc Sulfide $Cd_{0.6}Zn_{0.4}S$ thin films were deposited onto glass substrate at different substrate temperature (275-375)C^0 , at different Indium doping concentration (1-10) ml by spray pyrolysis technique , using precursor solution of Cadmium Chloride , Zinc Chloride , and Thiourea as Cadmium , Zinc and Sulfide source respectively The effect of Indium doping on the structure and morophology of prepared thin films have been investigeted .

X-ray diffraction (XRD) , scanning electron microscope (SEM) have been used examining these samples .XRD studies , have revealed that the films are polycrystalline , with preferentid orientation of the crystallites in film grown producing a strong hexagonal (002)or cubic (111) peak . the grain sizes were found in the rang of (175-339.68)nm and (214-258) nm depending on Indium dopinconcentration and annelingtemperature. And these results have been confirmed by scanning electron microscope .

The best crystallinity of the films was obtained at the substrate temperature of 350 C^0 and Indium doping concentration of5ml.

Keywords : *Indium doping ,$Cd_{0.6}Zn_{0.4}S$,SEM.*

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تأثير التطعيم بالانديوم على نمو وخصائص أغشية $Cd_{0.6}Zn_{0.4}S$ الرقيقة المرسبة بطريقة الرش الكيميائي

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الملخص

تم ترسيب اغشية رقيقة للمركب $Cd_{0.6}Zn_{0.4}S$ النقي والمطعم بالانديوم وذلك بطريقة الرش وعلى أرضية زجاجية بدرجات حرارية C^0(275-375) وبتراكيز ml (1- 10) من الانديوم وذلك بأستخدام محلول من $CdCl_2$ ، $ZnCl_2$، S على التوالي .

تم أستقصاء تأثير التطعيم بالانديوم على تركيب هذه الاغشية. استخدم طريقة حيود الاشعة السينية (XRD) والمجهر الالكتروني الماسح (SEM).ووجدت أن هذه الاغشية ذات تركيب متعدد البلورات مع قمة عند (002) سداسية التركيب و (111) مكعب التركيب . حجم الحبيبات وجدت عند مديات nm(339 - 175) وnm(258 - 214) معتمدا على نسبة الانديوم ودرجة حرارة التلدين على التوالي .

تم الحصول على أفضل خصائص تركيبية ذلك عند درجات حرارة (350) C^0 وعند تركيز ml(5) للأنديوم.

الكلمات الدالة : Indium doping ، $Cd_{0.6}Zn_{0.4}S$SEM ,

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1.INTRODUCTION

Cadmium Zinc Sulfide is ternary II-VI compound semiconductor polycrystalline. Thin films of $Cd_{1-x}Zn_xS$ are known to have properties in between those of Cadmium Sulfide and Zinc Sulfide.[1].$Cd_{1-x}Zn_xS$ thin films have been widely used as a wide band gap window material in hetrojunction photovoltaic solar cells.[2]. Oztas and Bedir (2001)[3], studied the structure, electronic and optical properties of Cd_{1-x} Zn_xSand Cd_{1-x} Zn_xS(In) fabricated by chemical spray method by using X-ray diffraction which shows a hexagonal(002) , (100) and (101) plane.

I lican et al .(2005),[4] studied X-ray diffraction of undoped and In-doped $Cd_{0.22}$ $Zn_{0.78}S$ films when produced by the spray pyrolasis deposition method at 275 ^oC substrate temperatures. This work describes the X-ray diffraction spectra of all films at room temperature and the films showed hexagonal and formed as $Cd_{0.22}Zn_{0.28}S$ polycrystalline structure.The aim of this research is the investigation the structural properties of the fabricated films befor and after In-doping with different concentration.

2.EXPERIMENTAL SET-UP

The chemical spray pyrolysis (CSP) technique offers an extremely easy way to prepare films with dopants, virtually any element in any proportion by merely adding it in the spray solution.

Undoped and In doped ($Cd_{0.6}Zn_{0.4}S$) thin films with required concentrations were deposited by spraying an aqueous solution. In order to distribute the sprayed solution regularly on the substrate to get uniform thickness of single layer films, the nozzle spray with constant spray rate 4 ml/min was fixed perpendicular to the hot heater plate. The distance between the nozzle and the hot plate was fixed at 28 cm. The nitrogen gas (N_2) is used as a carrier gas with pressure 2.5 bar. The spraying period is 7 secand stopping for 54 sec to avoid the excessive cooling of the substrate.The system is kept in an aluminum and glass chamber, and the chamber box is fitted with a fan to pull out the toxic gases produced during the decomposition of the spray solution. When the deposition completes, the heater switched off and the sample remains on the heated plate for about 90 min. or when substrate temperature $\leq$ 175 ^oC in order to occur the chemical interactions and the re-crystallization will be completed. Finally, the prepared films stored in the oven at a constant temperature of 25 ^oC.

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X-ray diffraction (XRD) is a commonly used technique for structure characterization of polycrystalline thin films by(PANalytical X–Ray diffractometer with CuKα radiation (λ=1.5406 A°) by using Braggs Law($n\lambda = 2\,d\sin\theta$).[5]

The scanning electron microscope (SEM) used to examinethe sample including external morphology, chemical composition, and crystalline structure and orientation of material making up the sample.[6]

3.RESULTS AND DISCUSSIONS

X-ray diffraction pattern was used to study all$Cd_{0.6}Zn_{0.4}S$ films were deposited at different substrate temperature (275 - 375) ^{o}C which show in the Figure.(1).

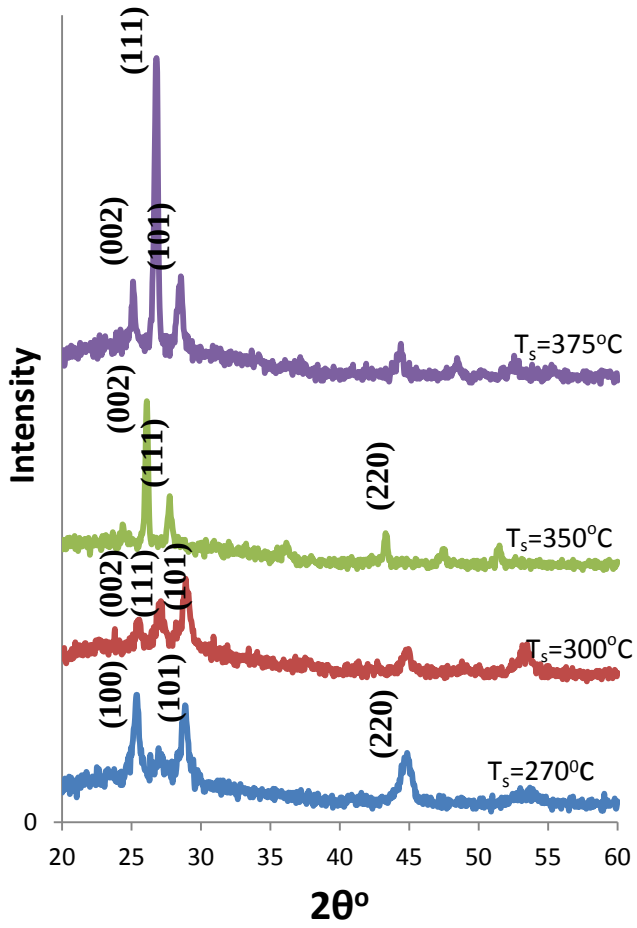

Figure.(1): XRD patterns of $Cd_{0.6}\,Zn_{0.4}S$ films deposited at different substrate temperatures.

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From this figures the determined structural parameters, such as peak position (2θ), Full Width Half Maximum (FWHM), interplanar spacing (d), intensity (Int.%), and miller indices (h k l) of the X-ray patterns for three strongest peak of$Cd_{0.6}Zn_{0.4}S$ thin films examined with the Inorganic Crystal Structure Database (ICSD) are summarized in Table.(1) below.

Table.(1): XRD results identify the determined structure parameters for $Cd_{0.6}Zn_{0.4}S$ films deposited at different substrate temperatures.

	measurement				ICSD slandered X-ray data base	
T_s °C	2θ°	d A°	FWHM	int.%	d A°	(h k l)
275	25.38	3.50	0.53	100	3.53	(1 0 0)
	28.82	3.09	0.62	93	3.10	(1 0 1)
	44.02	2.02	0.82	57	2.04	(2 2 0)
300	28.96	3.07	0.71	100	3.10	(1 0 1)
	27.08	3.28	0.81	64	3.27	(1 1 1)
	25.54	3.48	0.65	43	3.34	(0 0 2)
350	26.12	3.40	0.24	100	3.34	(0 0 2)
	27.76	3.21	0.31	31	3.27	(1 1 1)
	43.31	2.08	0.29	21	2.04	(2 2 0)
375	26.80	3.32	0.30	100	3.27	(1 1 1)
	28.50	3.12	0.43	23	3.10	(1 0 1)
	25.15	3.35	0.25	19	3.34	(0 0 2)

The XRD patterns of $Cd_{0.6}Zn_{0.4}S$ thin films show the (1 0 0), (0 0 2), and (1 0 1) diffractions which are related to hexagonal$Cd_{0.6}Zn_{0.4}S$ with a preferred orientation of (0 0 2), while the (111), and (2 2 0) are related to cubic$Cd_{0.6}Zn_{0.4}S$ with a preferred orientation of (1 1 1)

The peak intensity increase as the substrate temperature increase from 275 °C to 375 °C which indicates the increase in the degree of the crystalline of the films.

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The grain size (D), and dislocation density(ρ_d)were calculated for the dominated peak. And the results are shown in Table.(2).

$$D = \frac{0.94\lambda}{\beta\cos\theta}$$

$$(\rho_d) = (1/D^2)$$

Table.(2): XRD results identify the determined structure parameters for dominate peak of $Cd_{0.6}Zn_{0.4}S$ films deposited at different substrate temperatures.

T_s °C	Grain size (nm)	Dislocation (nm^{-2})
275	153.53	4.24E-05
300	115.29	7.52E-05
350	339.68	8.67E-06
375	272.13	1.35E-05

Figure.(2) shows the variation of the determined grain size and dislocation density versus the substrate temperature for as deposited $Cd_{0.6}$ $Zn_{0.4}$Sthin films. The maximum value of the films grain size and the lower value of the dislocation density were found at 350 °C substrate temperature, which indicated that the best crystalline of the films occurred at 350 °C.

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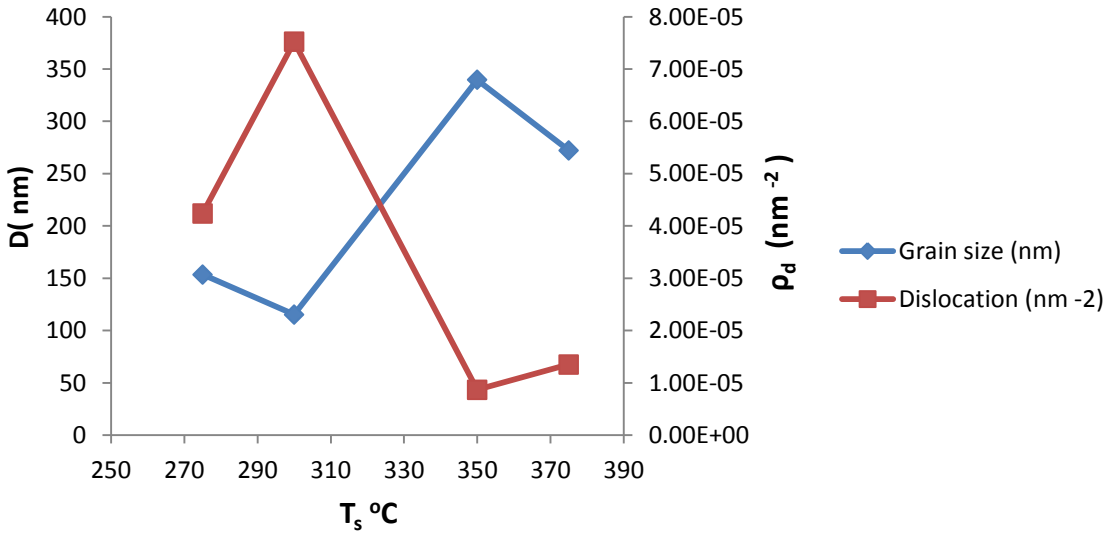

Figure.(2): Grain size and dislocation density for $Cd_{0.6}Zn_{0.4}S$ thin films deposited at different substrate temperature.

The scanning electronic microscope (SEM) images of the films deposited at substrate temperature 350 ^{o}C is shown in Figure.(3).

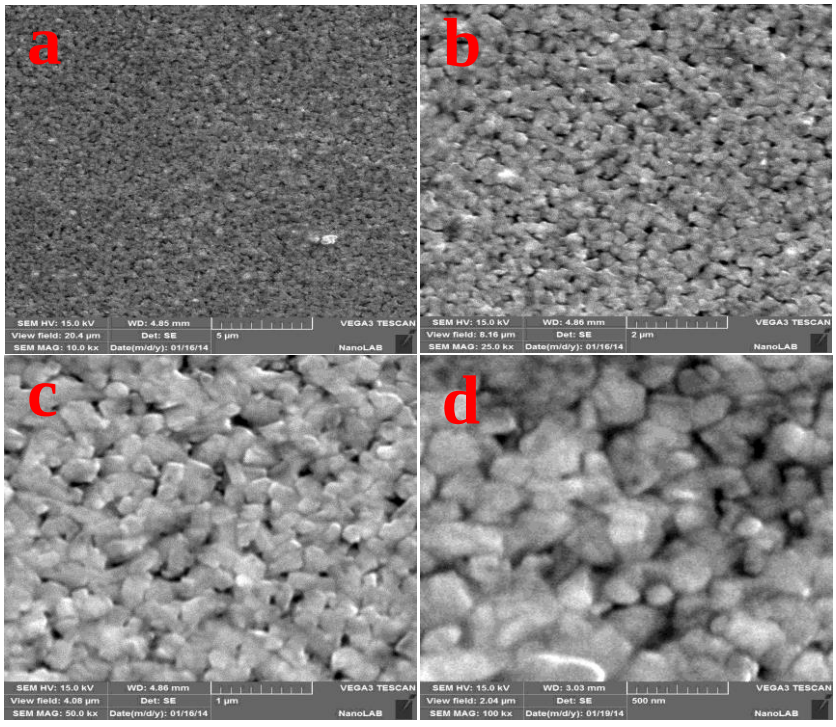

Figure.(3): SEM image of $Cd_{0.6}Zn_{0.4}S$ thin films prepared at substrate temperature 350 ^{o}C at different magnification a) 10000X, b) 25000X c)50000X, and d)100000X.

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The average diameter of grain was determined calculated at substrate temperature 350 ^{o}C is was found to be 242.72 nm as shows in Figure.(4).this result shows good aggrement with lary 2014. [7]

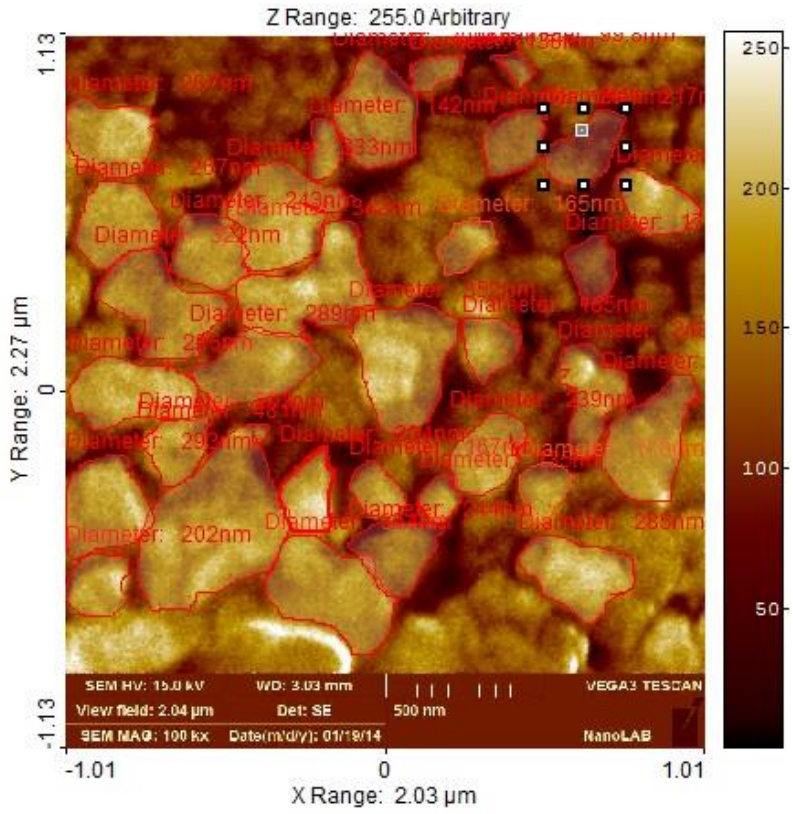

Figure.(4): SEM image of$Cd_{0.6}Zn_{0.4}S$ at magnification 100000X treated by SPIP software to measure the average grainsdiameter.

Also X-ray diffraction pattern was used to study the structure of all In-doped $Cd_{0.6}$ $Zn_{0.4}$Sfilms were deposited with different concentrations (1, 2.5, 5, 10) ml of Indium at constant substrate temperature (T_s= 350 ^{o}C). The XRD patterns of the prepared films are shown in Figure.(5) and Table.(3).

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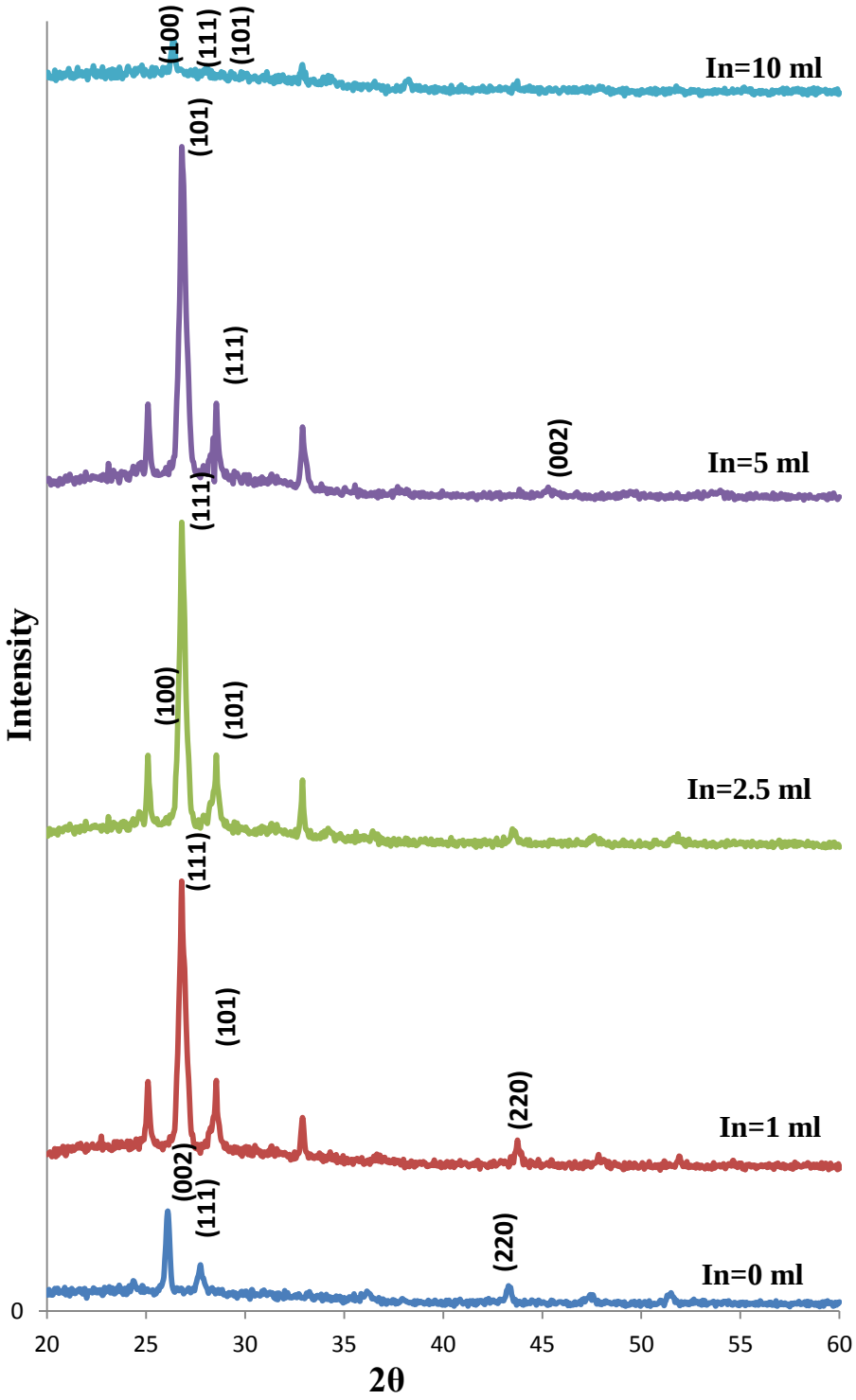

Figure.(5): XRD pattern of$Cd_{0.6}Zn_{0.4}S$:In thin films with different In concentrations deposited at substrate temperature 350 ^{o}C.

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Table.(3): XRD results identify the determined structure parameters for In-doped $Cd_{0.6}Zn_{0.4}S$ films deposited at substrate temperatures 350 ^{o}C.

Determined					ICSD slandered X-ray data base	
In ml	**2θ^{o}**	**d A^{o}**	**FWHM**	**int.%**	**d A^{o}**	**(h k l)**
1	26.95	3.30	0.33	100	3.27	(1 1 1)
	28.70	3.10	0.40	33	3.27	(1 0 1)
	44.64	2.02	0.34	22	2.04	(2 2 0)
2.5	26.90	3.31	0.35	100	3.27	(1 1 1)
	25.28	3.51	0.35	54	3.53	(1 0 0)
	28.62	3.11	0.35	29	3.10	(1 0 1)
5	29.01	3.07	0.40	100	3.10	(1 0 1)
	27.22	3.27	0.54	88	3.27	(1 1 1)
	44.92	2.01	0.43	48	2.00	(2 2 0)
10	29.11	3.06	0.488	100	3.10	(1 0 1)
	25.64	3.47	0.40	79	3.49	(1 0 0)
	27.21	3.27	0.44	59	3.27	(1 1 1)

It can be seen from Figure.(5) and Table.(3) that after doping the films with Indium, the main diffraction peak shifted to a higher angle from (26.95) for pure film prepared at substrate temperature 350 ^{o}C to (26.90) for the doped film doped with (1 ml) In concentration prepared at the same substrate temperature.

Also it can be seen from Figure.(5) that the peak intensity increase with increasing In-concentration and the highest peak intensity appear at 5 ml of Indium concentration

Indium doping caused reorientation which exhibit itself as (0 0 2) preferred orientation.

Scherer'sformulaandWilliamson-Hall equation were used to measure the grain size and dislocation density, respectively. The calculated parameters are shown in Table.(4).

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Table.(4): XRD results identify the calculated structure parameters for dominate peak of In-doped of $Cd_{0.6}Zn_{0.4}S$ films deposited with different In-concentratino at substrate temperature 350 ^{o}C.

In ml	Grain size (nm)	Dislocation (nm $^{-2}$)
0	339.68	4.24000E-05
1	258.47	1.49685E-05
2.5	243.67	1.68421E-05
5	214.18	2.17993E-05
10	175.59	3.2434E-05

Figure.(6) shows the variation of the determined values of the grain size and the dislocation density for the films doped with different In concentrations and prepared at substrate temperature of 350 ^{o}C.

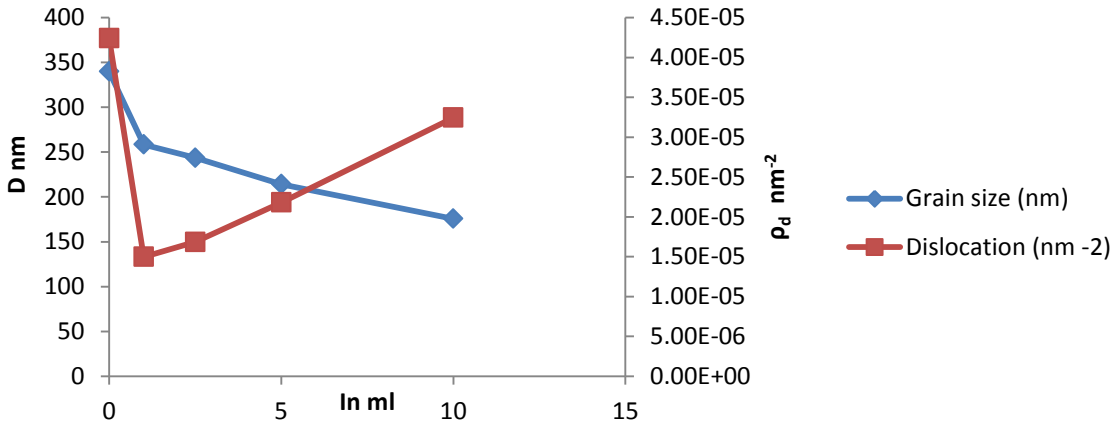

Figure.(6): Grain size and dislocation density as a function of In-doped$Cd_{0.6}Zn_{0.4}S$ thin film at different In-concentrations.

It is clear from the result of this figure, the grain size decreased with In doping concentration, while the dislocation density increased, the decries of the grain size of$Cd_{0.6}$ $Zn_{0.4}S$ films by doping with In may be due to the structural modification films after doping , or may be due to the

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formation of secondary phases. It can suppose that the indium ions can replace either substitution the cadmium or zinc ions in $Cd_{0.6}Zn_{0.4}S$ lattice creating the structural deformation.

Figure.(7) shows the SEM images of pure and 5ml indium doped $Cd_{0.6}Zn_{0.4}S$thin films prepared at substrate temperature 350 ^{o}C. These images showed noticeable change in the surface morphology after doping with indium, where the grain size of the films decreased after doping with homogenous dislocation of the grains

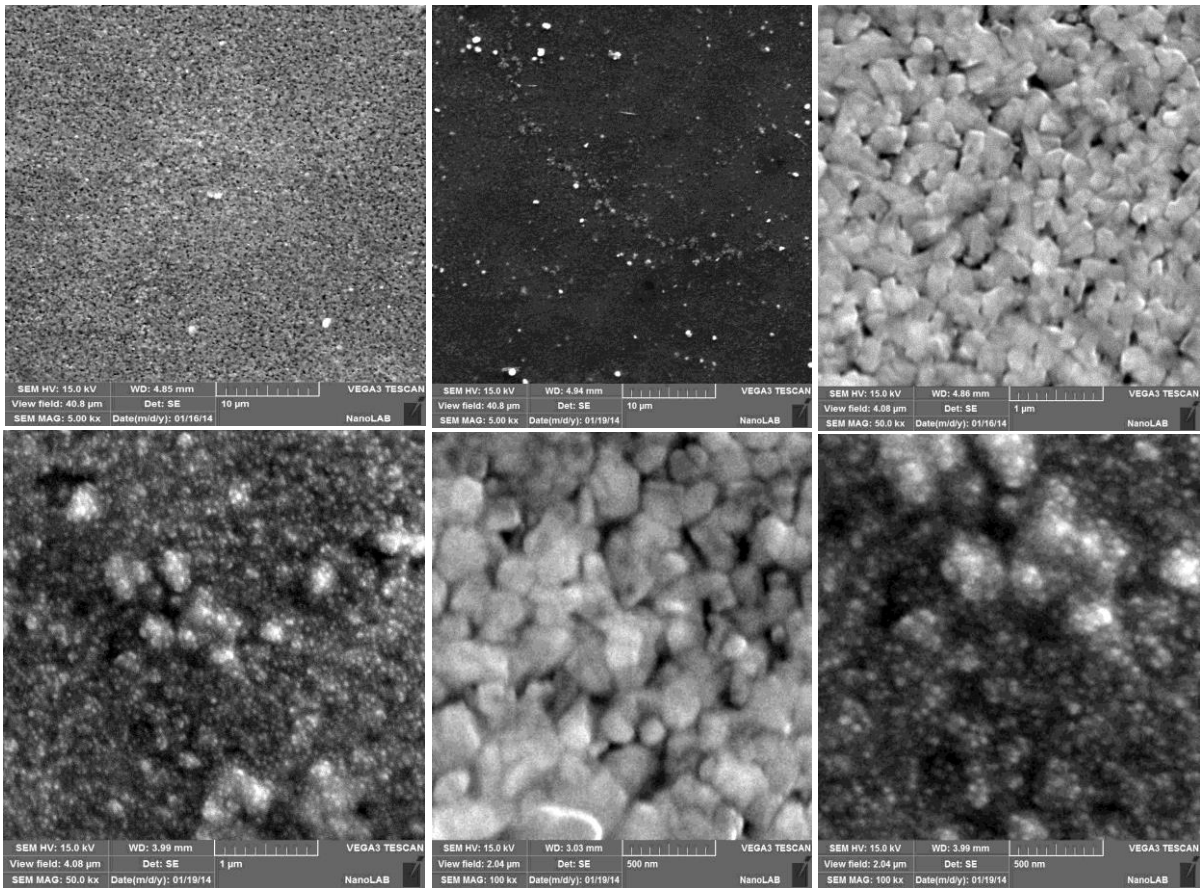

Figure.(7): SEM image of $Cd_{0.6}Zn_{0.4}S$ films for pure(on left) and In-doped (5ml) (at right), at different magnification, 5 000X, 50 000X, and 100 000X from top to bottom

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When the grains are very small, it is unable to measure the grains size by using shape tool, in this case cross section analysis tool was used to measure the average diameter of grains as shown in Figure.(8) indicated that the most of the grains have diameter (grain size) less than 100 nm.The same results get by reference[4].

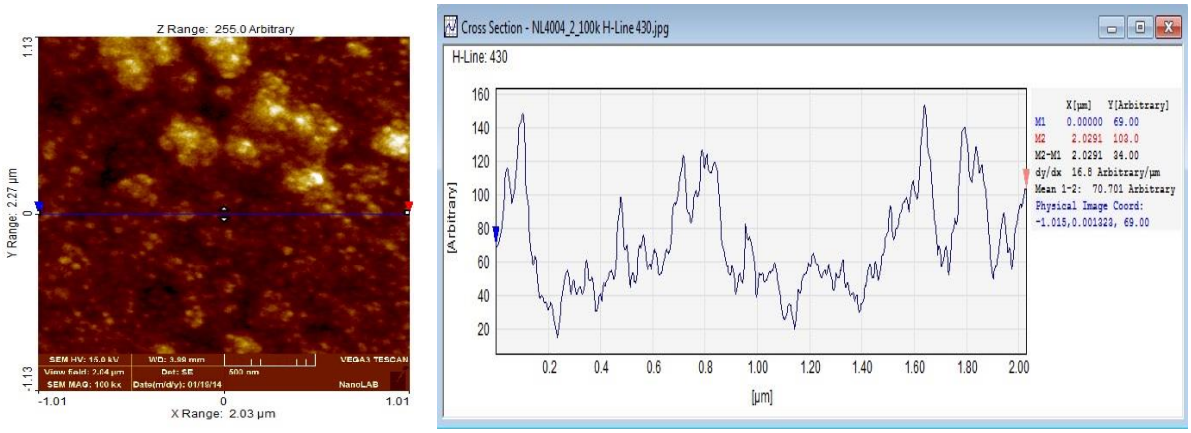

Figure.(8): SEM images of$Cd_{0.6}Zn_{0.4}S$:In thin films prepared at 350 ^{o}C with 5 ml In-concentration. The right side part of the image represents the cross section marked by dashed lines.

4.CONCLUSIONS

The XRD study confirms the polycrystalline structure with hexagonal and cubic phases of the films. The intensity of (0 0 2) peak is found to be improved for the films with substrate temperature and the maximum intensity was found at substrate temperature of 350 ^{o}C. The bigger size of the grain was found at substrate temperature of 350 ^{o}C.The Indium doping to the films causes a noticeable change in the films structure compared to the undoped one, where the crystal nature of the films was improved with indium doping. The preferential orientation of the films changed from (1 1 1) to (1 0 1), and the grain size decreased with increasing Indium doping.

5.SUGGESTION FOR FUTURE WORK

studyelectrical properties of the prepared $Cd_{0.6}Zn_{0.4}S$ thin films and effects of In-doped and annealingtemperature on these propertie .

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