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The Role of Al Doping and Annealing Temperatures on Structural Properties of Nano Thin CdS Films Prepared by PLD

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ABSTRACT

Pure and Al doped cadmium sulfide (CdS) thin films with different doping ratios (1, 3, 5 and 7) % have been deposited onto glass substrates using pulsed laser deposition technique ,then annealed films at different annealing temperatures (300, 373, and 473) K. The effect of Al doping on structural properties of the all prepared thin CdS films of thickness (410 ± 5 nm) was investigated. The structural properties of the thin films have been studied using X-ray diffraction (XRD). The polycrystalline films with a hexagonal structure for pure and Al doped CdS have been obtained .The crystallite size of prepared films are found to be in nano-metric range. The structure of prepared films was found to be strongly dependent on Al doping concentration and annealing temperatures.

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INTRODUCTION

In recent years, there has been growing interest in II–VI semiconductor materials for their potential applications in optoelectronic and photovoltaic industries. One of the most promising alternative materials is a cadmium sulfide (CdS) thin film, which is inorganic group and a chalcogenide n-type semiconductor having a direct energy band gap between 2.28eV and 2.45eV (Mohamed, H.A., 2014, Husham, M., 2014; Kwon, J.H., 2013). CdS films have interested structural, optical and electrical properties that are much different compared to bulk materials. These films can be applied to many technologies such as window layer in solar cells, optical sensors, transistors], diodes etc. Various methods such as electro- deposition, spray pyrolysis, successive ionic layer adsorption and reaction (SILAR), pulsed laser deposition vacuum evaporation and chemical bath deposition (CBD), etc. are used to obtain thin CdS films. Among these techniques pulsed laser deposition technique is favored and versatile because of its relatively simple growth technique, inexpensive and scalable technique for the deposition of high quality and large area films. In this work pulsed laser deposition (PLD) technique is used for preparation pure and Al doped CdS thin films. These films possessed nanostructures under optimized conditions of variety of materials.

The aim of the present work is to study the effect of Al doping and the annealing temperatures on structural properties of thin CdS films prepare by pulsed laser deposition technique.

MATERIAL AND METHODS

Pure CdS powder and doped with different Al doping ratios(1, 3, 5 and 7) % with high purity (99.999%) which have been pressed under 5 Ton to form target with dense and homogenous good quality deposit with 1cm diameter and 0.2 cm thickness.The pulsed laser deposition (PLD) technique was employed to produce pure and Al doped thin CdS films with 420±5nm thickness and various doping ratio deposited on cleaned glass substrates .The pulsed laser deposition technique is carried out inside chamber generally at 10^{-3}Torr vacuum conditions and low pressure of a background gas for specific cases of oxides and nitrides. The specifications of used laser are Nd: YAG laser (HuafeiTongda Technology—DIAMOND-288 pattern EPLS), power= 700 MJ, f= 6 HZ, λ= 1064 nm and 800 pulse number of shots. The substrate was placed in front of the target with its surface parallel to that of the target. Sufficient gap was kept between the target and the substrate so that the substrate holder does not obstruct the incident laser beam. Clean glass slides which were used to study the structural property of prepared pure and Al doped CdS thin films at

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different doping ratio and annealed all prepared films under vacuum (10^{-3}Torr) with different annealing temperatures (300, 373, and 473) K. The present work was used X-ray diffraction type Shimadzu (power diffraction system with Cu-K_α X-ray tube (λ = 1.54056 Å) was used with 2θ scan values of 20° and 60°.

RESULTS AND DISCUSSION

Figures (1 - 3) show X-ray diffraction patterns for pure and Al doped CdS thin films with different doping ratios (1, 3, 5 and 7) % and annealing temperatures (300, 373, and 473) K were deposited on glass substrates.

In general from the diffraction patterns of these figures, it can be seen that there are some sharp diffraction peaks and clear defined which indicated that the films have polycrystalline structure with the hexagonal phase. The degree of crystallinity for CdS films decreases gradually with increasing the ratio of the Al (i.e., decrease in intensity). These values of CdS were closed well with that data of standard values (JCPDS file no.96-901-1664). Relevant parameters for the obtained CdS thin films with hexagonal polycrystalline structure were presented in Tables (1-3).

Figure (1) shows the diffraction patterns of un annealed (300K) pure and Al doped thin CdS films. For the pure films, three peaks are appeared at 2θ equal to 24.838, 26.543, 28.202 which assigned to the (100), (002), and (101) planes respectively. The relatively stronger peak along (002) film structure has been observed. These orientations correspond to the hexagonal phase for CdS film. Similar results have been reported by other researches.

The full width at half maximum (FWHM) of the peak (in radians), is a measure of the size of the crystallite in a polycrystalline film, *C.S*, as described by Scherrer's formula (Warren, B., 1969):

$$C.S = \frac{0.94\,\lambda}{FWHM\,.\,\cos(\theta)} \quad (1)$$

where θ is the Bragg angle and λ is the X-ray wavelength. The crystallite size values were equal to 16.1, 12.7, 13.6, 17.7 and 13.6 nm for professional peak as shown in Table (1). This clearly indicates the nano-crystalline nature of resultant films deposited at different Al doping.

Lattice parameters a and c for the hexagonal structure was found by the following equation, where both spacing lattice (d_{hkl}) and miller indices (hkl) are known:

$$\frac{1}{d_{hkl}} = \frac{4}{3}\frac{h^2+hk+k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$

The lattice parameter values a, and c are a = 4.135 Å and c = 6.699 Å which are in agreement with the JCPDS data (80-006), (JCPDS, 2000).

Another noticeable remark from figure (1) is that the number of peaks for doped thin CdS film with 1% Al exceeded than that for pure CdS film and the peak height increased with the increasing doped ratios of Al. This increase is due to decrease the size of the crystallite, as well as doped Al is working to increase the crystallization of films. All these structured parameters are tabulated in Table (1).

Fig.(2) and Table (2) illustrate the XRD pattern and structural parameters for pure and doped CdS films annealed at 373K.The results of XRD for prepared films annealed at 373K obtained that the increase in the high and sharp of the peaks (decrease in the full-width at half-maximum (FWHM)) and increasing in the crystal structure of CdS films. This means that the annealing caused decreasing in the crystal defects due to prepare thin films and the interplaner surface defects which gave the material atoms perfect energy to return and arrangement itself in crystal lattice and release from the stresses which cause for the lattice thermal mismatch.

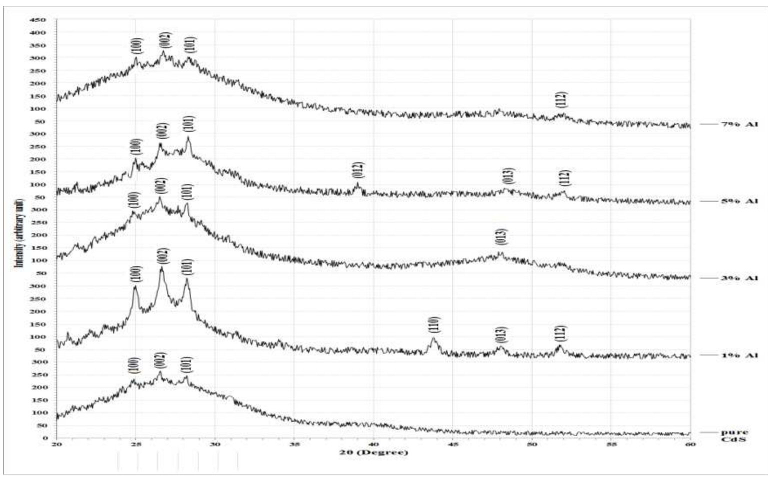

Fig. 1: X-ray diffraction patterns of unannealed (300 K) deposited pure and Al doping CdS films with different doped ratios.

Table 1: Structural parameters: 2θ, d_{hkl}, (hkl), FWHM, C.S,a and c of deposited unannealed (300 K) pure and Al doped CdS films with different doping ratios.

Al %	2θ	d_{hkl}Exp	d_{hkl}Std.	hkl	FWHM	C.S. (nm)	a (Å)	c (Å)
	24.8387	3.5817	3.5827	(100)	0.3687	22.1	4.13580	6.71074
0	26.5438	3.3554	3.3572	(002)	0.5069	16.1		
	28.2028	3.1617	3.1609	(101)	0.4147	19.7		
	24.8734	3.5768	3.5827	(100)	0.4147	19.6	4.13012	6.69567
	26.6046	3.3478	3.3572	(002)	0.6452	12.7		
1	28.2029	3.1616	3.1609	(101)	0.5060	16.2		
	43.7788	2.0662	2.0685	(110)	0.8295	10.3		
	48.0184	1.8932	1.8982	(013)	0.7834	11.1		
	51.7512	1.7650	1.7611	(112)	0.7373	12.0		
	24.9026	3.5727	3.5827	(100)	0.4608	17.7	4.12535	6.68997
3	26.6277	3.3450	3.3572	(002)	0.5991	13.6		
	28.2028	3.1617	3.1609	(101)	0.4147	19.7		
	48.0186	1.8932	1.8982	(013)	0.5069	17.2		
	24.9770	3.5622	3.5827	(100)	0.4147	19.6	4.11326	6.68601
	26.6438	3.3430	3.3572	(002)	0.4608	17.7		
5	28.2949	3.1516	3.1609	(101)	0.3226	25.4		
	38.9862	2.3084	2.4498	(012)	0.7373	11.4		
	48.2949	1.8830	1.8982	(013)	0.7834	11.1		
	51.9816	1.7578	1.7611	(112)	0.6452	13.7		
	25.0230	3.5557	3.5827	(100)	0.4608	17.7	4.10581	6.66529
7	26.7281	3.3326	3.3572	(002)	0.5991	13.6		
	28.3049	3.1505	3.1609	(101)	0.7834	10.5		
	51.9816	1.7578	1.7611	(112)	0.7373	12.0		

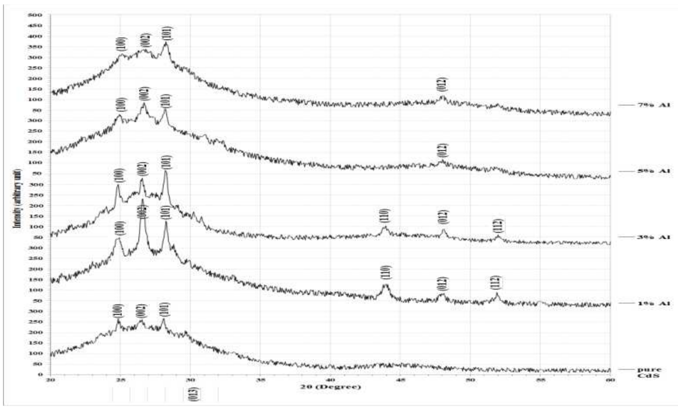

Fig. 2: X-ray diffraction patterns of deposited pure and Al doped CdS films with different doping ratios at 373K.

Table 2: Structural parameters: 2θ, d_{hkl}, (hkl), FWHM, C.S,a and c of deposited pure and Al doped CdS films with different doping ratios at 373K.

Al %	2θ	d_{hkl} Exp.	d_{hkl} Std.	hkl	FWHM	C.S. (nm)	a (Å)	c (Å)
	24.8385	3.5817	3.5827	(100)	0.3687	22.1	4.13583	6.73370
0	26.4516	3.3669	3.3572	(002)	0.5991	13.6		
	28.1106	3.1718	3.1609	(101)	0.3226	25.4		
	24.8387	3.5817	3.5827	(100)	0.6452	12.6	4.13580	6.73370
	26.5421	3.3497	3.3572	(002)	0.4608	17.7		
1	28.2488	3.1566	3.1609	(101)	0.3687	22.2		
	43.9313	2.0579	2.0685	(110)	0.6452	13.3		
	47.9724	1.8949	1.8982	(012)	0.5991	14.5		
	51.8433	1.7621	1.7611	(112)	0.4608	19.2		
	24.8387	3.5817	3.5827	(100)	0.4147	19.6	4.13580	6.70578
	26.5638	3.3554	3.3572	(002)	0.3226	25.3		
3	28.2528	3.1617	3.1609	(101)	0.3687	22.2		
	43.9397	2.0620	2.0685	(110)	0.5069	16.9		
	48.1106	1.8898	1.8982	(012)	0.3687	23.6		
	51.9816	1.7578	1.7611	(112)	0.5530	16.0		
	24.9309	3.5687	3.5827	(100)	0.5530	14.7	4.12075	6.67660
5	26.6820	3.3383	3.3572	(002)	0.6452	12.7		
	28.2028	3.1617	3.1609	(101)	0.3687	22.2		
	48.0184	1.8932	1.8982	(012)	0.5530	15.7		
	25.1613	3.5365	3.5827	(100)	0.7834	10.4	3.84821	6.32331
7	26.7281	3.3326	3.3572	(002)	0.6912	11.8		
	28.2028	3.1617	3.1609	(101)	0.5530	14.8		
	48.0184	1.8932	1.8982	(012)	0.5991	14.5		

Figure (3) and Table (3) show the XRD pattern and structural parameters for pure and doped CdS films annealed at 473K.Also this figure shows the number of peaks for doped thin CdS films with 1% Al exceeds than pure films. This refer to the doped CdS samples retain the hexagonal structure. This illustrates that the degree of crystallinity for CdS samples which increased by increasing the doping ratio to 1% then decreased gradually by increasing Al ratios to 3%, 5% and 7%. It had been observed that the full-width at half-maximum (FWHM) of the main peak decreased as a function of ratios doped, and this is associated with the variant of the crystal size in CdS films. Similar results have been observed for CdS films prepared by different techniques.

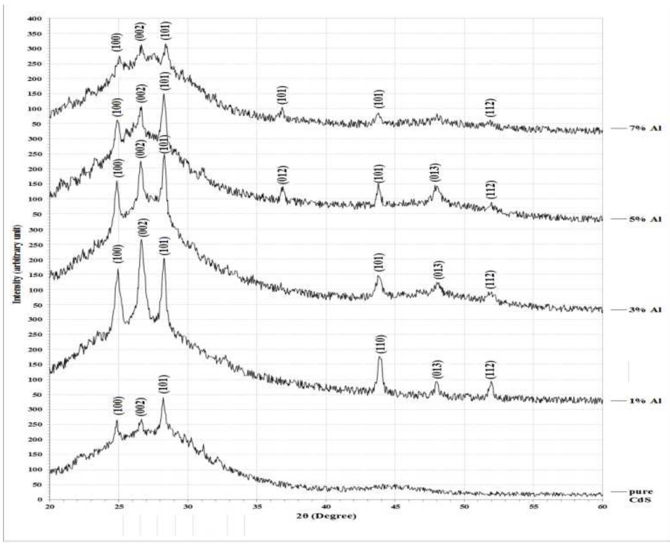

Fig. 3: X-ray diffraction patterns of annealed (473 K) pure and Al doped CdS films with different doping ratios.

Table 3: Structural parameters: 2θ, d_{hkl}, (hkl), FWHM, C.S, a and c of annealed (473K) pure and Al doped CdS films with different doping ratios.

Al %	2θ	d_{hkl} Exp.	d_{hkl} Std.	Hkl	FWHM	C.S (nm)	a(Å)	c(Å)
	24.8387	3.5817	3.5827	(100)	0.3687	22.1	4.13580	6.69932
0	26.5899	3.3497	3.3572	(002)	0.3687	22.1		
	28.2028	3.1617	3.1609	(101)	0.4147	19.7		
	24.8309	3.5828	3.5827	(100)	0.5069	16.0	4.13708	6.70029
	26.5859	3.3501	3.3572	(002)	0.5530	14.8		
1	28.2028	3.1617	3.1609	(101)	0.3687	22.2		
	43.8710	2.0620	2.0685	(110)	0.3226	26.5		
	47.9263	1.8966	1.8982	(013)	0.3226	27.0		
	51.9355	1.7592	1.7611	(112)	0.3687	24.0		
	24.8387	3.5817	3.5827	(100)	0.4147	19.6	4.13580	6.69932
	26.5899	3.3497	3.3572	(002)	0.3687	22.1		
3	28.2949	3.1516	3.1609	(101)	0.3226	25.4		
	43.7327	2.0682	2.0685	(110)	0.5069	16.9		
	48.0645	1.8915	1.8982	(013)	0.6452	13.5		
	51.8894	1.7607	1.7611	(112)	0.6912	12.8		
	24.8848	3.5752	3.5827	(100)	0.3687	22.1	4.12826	6.69932
	26.5899	3.3497	3.3572	(002)	0.3226	25.3		
	28.2488	3.1566	3.1609	(101)	0.3687	22.2		
5	36.8664	2.4361	2.4498	(012)	0.3687	22.7		
	43.7788	2.0662	2.0685	(110)	0.2765	31.0		
	48.0184	1.8932	1.8982	(013)	0.5991	14.5		
	51.9816	1.7578	1.7611	(112)	0.4608	19.2		
	25.0691	3.5493	3.5827	(100)	0.5530	14.7	4.09838	6.68794
	26.6359	3.3440	3.3572	(002)	0.5530	14.8		
7	28.3871	3.1415	3.1609	(101)	0.4608	17.8		
	36.8203	2.4391	2.4498	(012)	0.5991	14.0		
	43.7788	2.0662	2.0685	(110)	0.5069	16.9		
	51.8894	1.7607	1.7611	(112)	0.5069	17.4		

Conclusions:

From the data of the present work, we can conclude that :

- All prepared and annealed pure and Al doped thin CdS films by pulsed laser deposition on glass substrate have polycrystalline structure with the hexagonal phase.
- The (002) and (101) plane are main for prepared films.
- The values for the crystallite size are found to be in nano metric range.
- Lattice constants of prepared pure CdS thin films nearly decreasing when Al doping ratio increased.

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