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Effect of Li and Al Dopingon the Structural, Morphological and Some Optical Properties of CdS Thin Films Fabricated by Chemical Bath Deposition

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Abstract: Pure and doped CdS by 2.5, 5, 7.5 vol.% Li and Al thin films were prepared by chemical bath deposition method with thicknesses (150, 300, 450) ±20 nm and annealed at 573 K for 1 h. X-ray diffraction analysis revels that pure and doped films crystallize in polycrystalline cubic structure with a preferred orientation along the 111 plane. The morphology of the films was studied by SEM and AFM. The surface morphology of CdS are best homogeneous and less pores after doping with Li and Al. UV-VIs spectra were obtained for the films before and after annealing. The values of optical transmittance and the optical energy gap of the films qualify them features to work as filters and antireflection coating to improve solar cell efficiency. The values of optical energy gap of pure and doped CdS by 2.5, 5, 7.5 vol.% Li and Al thin films were equal to (2.89, 2.81, 2.79, 2.72) eV and (2.89, 2.85, 2.79, 2.81) eV, respectively.

Key words: CdS, Al, Li thin films, structural and optical properties, CBD, morphology

INTRODUCTION

The term thin films is called a layer or a number of layers of materials that does not exceed 1 μm (Chopra, 1969; Heavens, 1970). The study of the properties of the material in the form of thin films have attracted the attention of physicists at the beginning of the 19th century where many important research has been prepared in this field, working this thin films development resulted many semiconductors were used in the preparation of thin (Al-Ameen, 1996.; Segger, 1973). The cadmium sulfide CdS is a semiconductor material belong to group (2-6) in the periodic table. The crystalline structure of this material is the cube (zinc blende) or hexagonal (wurtzite) (Sadao, 2005). The unit cell is of a type centered faces (Singh *et al*., 2011). Cadmium sulphide has a very suitable direct energy gap 2.42 eV to applications in solar cells, especially as a window material (Al-Ani, 1977). The CdS crystal possesses the yello wish color of the orange (Heavens, 1970; Gupta *et al*., 1978). The most important applications are its use in solar cells and photovoltaic reagents, it is easy to prepare, inexpensive and highly stable. In this research, we reported about the preparation of nanocrystalline CdS thin films and discuss about the effect of volume percentage of Li and Al doping on structural and some optical properties of the prepared CdS thin films.

MATERIALS AND METHODS

Experimental details: Thin film of cadmium sulphite CdS and Li, Al doped CdS nanostructure were grown on ultrasonically cleaned glass substrate by using (CBD) technique. The weight of substrate and the films were calculated by using digital balance sensitive 10^{-4} g.

The CdS films were prepared using aqueous solutions of cadmium acetate $Cd(CH_3COO)_2.H_2O$; 0.025 M (its molecular weight 266.53 g/mol and purety 98.0% supplied by CDH-India), thiourea $(NH_2)_2$ CS; 0.05 M (its molecular weight 76.12 g/mol and purety 98.0% supplied by CDH-India) and ammonia NH_3 (25%). Al doped CdS films were prepared by adding 1.575 g of aluminum sulphate $Al_2(SO_4)_3$. $16H_2O$ 0.025 M dissolved in 100 mL de-ionized water (its molecular weight 630.38 g/mol and purity 99.5% supplied by CHD India). Li doped CdS films were prepared by adding 0.211 g of Li thium chloride Li Cl (0.1M) dissolved in 50 mL de-ionized water (its molecular weight 42.39 g/mol and purity 99.5% supplied by Fluka-Switzerland). All films were deposited with different volume percentage (2.5, 5, 7.5) from both solvents as shown in Table 1. In this modality the chemical bath solution is stirred meanwhile glass substrates are immersed vertically into the bath. Both solution (in the case of doping aluminum or lithium) is maintained at 348 K, pH 9.5 and the thickness of the films are (150, 300, 450) ±20 nm.

Table 1: The volume ratios of the solutions used to prepare the thin films

Cd $(CH_3COO)_2.2H_2O$ (0.025 M) $(NH_2)_2CS$ (0.05 M) (mL)	$Al_2(SO_4)_3.16H_2O$ (0.025 M) or LiCl (0.1 M) (mL)	The percentage of the defect
400	0	0
390	10	2.5
380	20	5
370	30	7.5

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Samples were tested with X-ray diffraction type (Shimadzu Japan XRD 6000) to identify the crystal structure of the prepared films, the crystallite size (D) was calculated from Scherrer's Eq. 1 (Culity, 1978):

$$D = \frac{k\lambda}{B\cos\theta} \quad (1)$$

Where:

K = Scherer constant and that amount is equal to $[2(\ln 2/\pi)^{1/2} = 0.94]$
λ = Wavelength
B = Full width at half maximum

Calculation of the lattice constants for cubic structure according to the following Eq. 2 (Kittel, 1976):

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \quad (2)$$

Where:

d_{hkl} = The distance between crystalline plans
hkl = Miller indices

The analysis of the surface topography of the samples done by Scanning Electron Microscope device (SEM) type (manufacturer: FEL, Quanta 450). Surface morphology was analyzed by Atomic Force Microscope (AFM) device type (SPM AA3000/Angstrom Advanced Inc.). Optical spectrums of the films were recorded by UV-visible 1800 spectra photometer. The absorption coefficient (α) determine according to the following Eq. 3 (Pankove, 1971):

$$\alpha = 2.303\frac{A}{t} \quad (3)$$

Where:

A = The absorption
t = Film thickness

The optical band gap E_g^{opt} was calculated by the following relation (Pankove, 1971):

$$\alpha h\upsilon = B(h\upsilon - E_g^{opt})^r \quad (4)$$

Where:

hυ = Photon energy
B = Constant depends on the nature of the material
r = The value depends on the nature of the transition

RESULTS AND DISCUSSION

Structural properties: Figur 1-3 show the XRD patterns of monochromatic Cu Kα line (λ = 1.5405 Å) of pure anddoped CdS by 2.5, 5, 7.5 vol.%, Li and Al thin films, grown on ultrasonically cleaned glass substrates at 348 K, and annealed to annealing temperatures 573 K in digital furnace for duration times 1 h, respectively. The peaks from the diffraction patterns were found to be characteristic topure and CdS: Li or Al thin films compared with standard ICD card No. 00-010-0454. All films exhibit peaks related to polycrystalline cubic structure with preferential orientation of 111 plane.

Figure 2 and 3, the X-ray spectra of CdS thin films shows an increase in the intensity of the peaks with the increase in doping concentration and after annealing

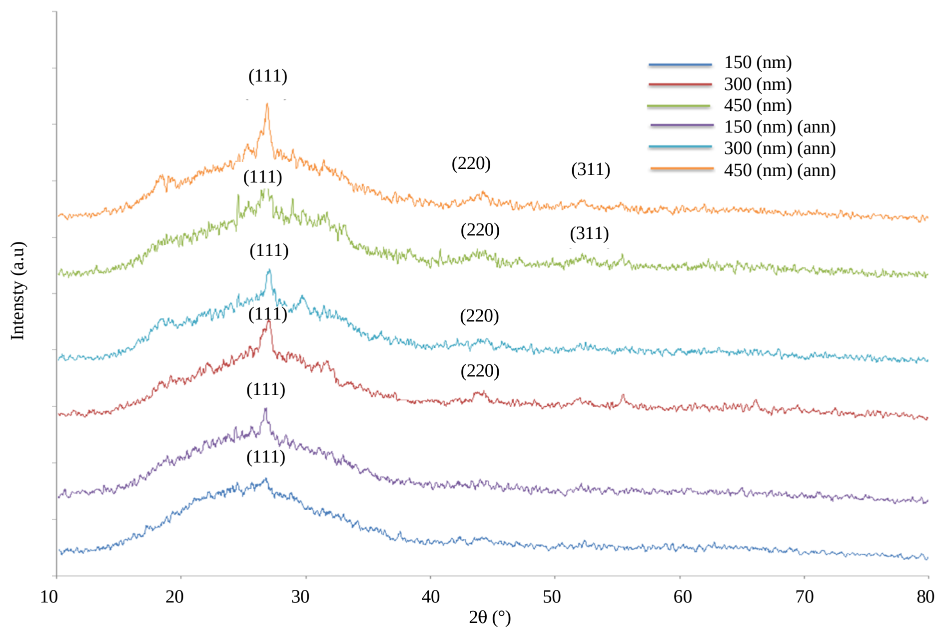

Fig. 1: XRD pattern of deposited CdS before and after annealing

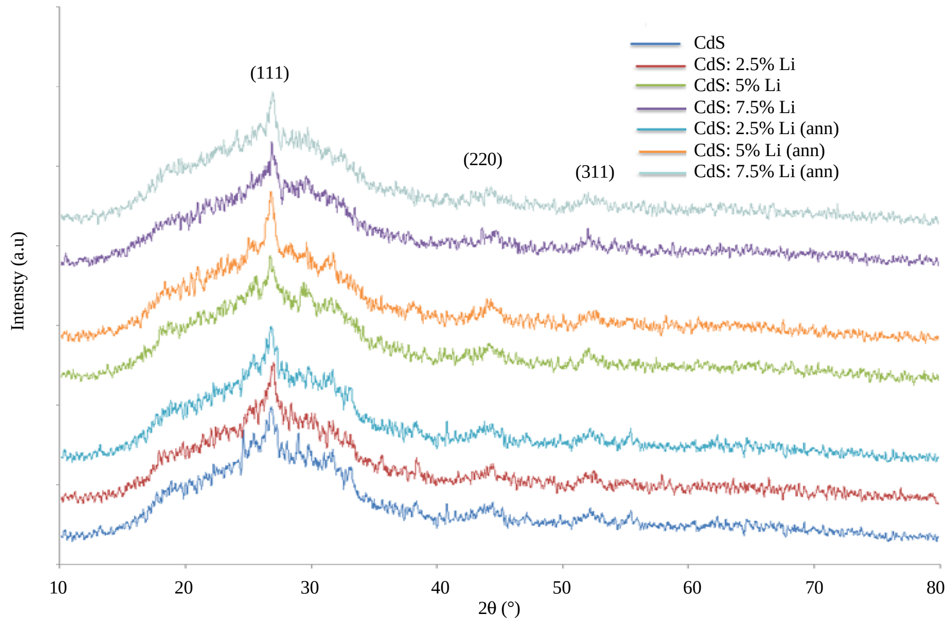

Fig. 2: XRD pattern of deposited CdS: Li before and after annealing

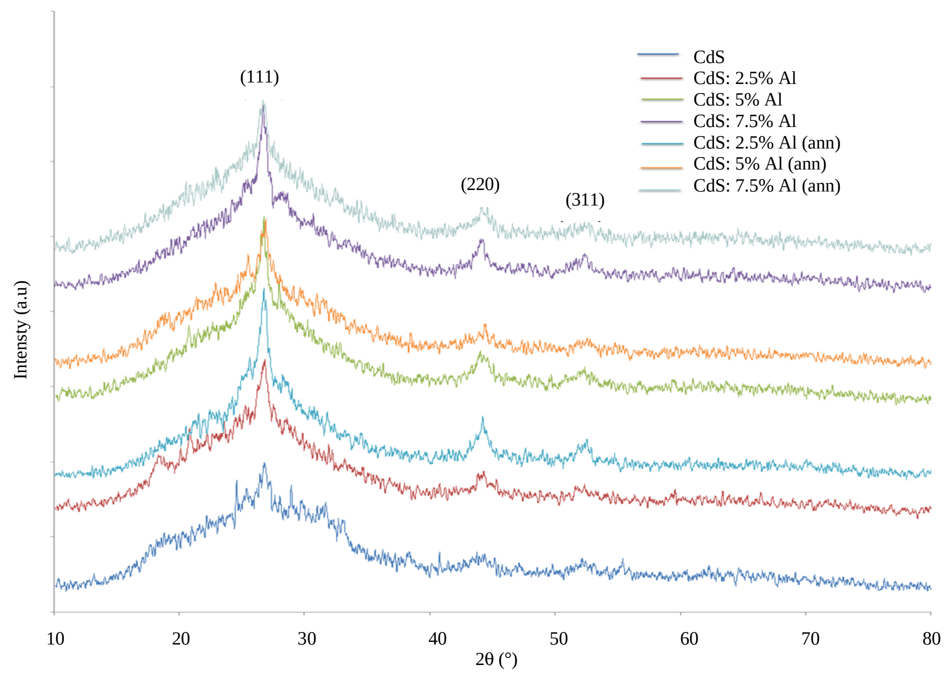

Fig. 3: XRD pattern of deposited CdS: Al before and after annealing for thickness (450 nm)

temperatures as illustrated in Table 2. Similar results have been earlier reported by Kavitha *et al*. (2016), Tepantlan *et al*. (2008) and Jafari *et al*. (2010). The diffraction peaks slightly shifted towards higher 2θ values with Li and Al doping which is confirms that the doped Li and Al substitutes Cd in CdS samples as illustrated in Table 3. This may be due to the smaller ionic radius of Li^{+1} (0.76Å) and Al^{+3} (0.57 Å) (Chung, 2001; Grjotheim and Welch, 1988) when compared with that of Cd^{+2} (0.97 Å). Apart from these peaks, no diffraction peaks of metallic, impurity phase like CdO or Al_2O_3 or Li_2O are detected in all the CdS pattern with Li and Al doping which imply that these atoms are solved successfully in the CdS host structure.

Table 2: XRD results of CdS thin films before and after annealing

Materials	Thickness (nm)	2θ (°)	d(Å) observed	d(Å) standard	FWHM	(hkl)	Average crystalline size (nm)
CdS	150	26.35	3.37	3.35	1.45	(111)	5.87
CdS	300	26.82	3.32	3.35	0.95	(111)	8.97
		43.90	2.06	2.07	0.70	(220)	
CdS	450	26.75	3.32	3.35	0.82	(111)	10.39
		44.12	2.05	2.07	0.66	(220)	
		52.10	1.75	1.76	0.40	(311)	
CdS (ann.)	150	26.69	3.33	3.35	0.78	(111)	10.92
CdS (ann.)	300	26.96	3.3	3.35	0.72	(111)	11.84
		43.87	2.06	2.07	0.24	(220)	
CdS (ann.)	450	26.79	3.32	3.35	0.54	(111)	11.79
		44.21	2.04	2.07	0.28	(220)	
		52.21	1.75	1.76	0.30	(311)	

Table 3: XRD result of CdS: Al, Li thin films before and after annealing

Materials	Thickness (nm)	2θ (°)	d(Å) observed	FWHM	(hkl)	Average crystalline size (nm)
CdS: Li 2.5%	450	26.84	3.31	0.880	(111)	8.69
		44.32	2.04	0.420	(220)	
		51.56	1.77	0.200	(311)	
CdS: Li 5%	450	26.74	3.33	0.810	(111)	9.52
		44.11	2.05	0.560	(220)	
		51.95	1.75	0.580	(311)	
CdS: Li 7.5%	450	26.88	3.31	0.760	(111)	11.22
		44.61	2.02	0.600	(220)	
		52.04	1.75	0.440	(311)	
CdS: Li 2.5% (ann)	450	26.77	3.32	0.820	(111)	10.39
		44.01	2.05	1.040	(220)	
		52.19	1.75	0.260	(311)	
CdS: Li 5% (ann)	450	26.75	3.32	0.780	(111)	10.93
		44.17	2.04	0.870	(220)	
		52.19	1.75	0.340	(311)	
CdS: Li 7.5% (ann)	450	26.86	3.31	0.670	(111)	12.72
		44.25	2.04	0.600	(220)	
		51.83	1.76	0.500	(311)	
CdS: Al 2.5%	450	26.63	3.34	1.020	(111)	9.35
		44.10	2.05	0.780	(220)	
		51.72	1.76	0.320	(311)	
CdS: Al 5%	450	26.72	3.33	0.960	(111)	9.88
		44.07	2.05	0.840	(220)	
		52.26	1.74	0.760	(311)	
CdS: Al 7.5%	450	26.64	3.34	0.925	(111)	10.21
		44.13	2.05	0.720	(220)	
		52.38	1.74	0.160	(311)	
CdS: Al 2.5% (ann.)	450	26.67	3.33	1.020	(111)	10.35
		44.14	2.05	0.940	(220)	
		52.26	1.74	0.920	(311)	
CdS: Al 5% (ann.)	450	26.78	3.32	1.000	(111)	10.52
		44.3	2.04	0.620	(220)	
		52.44	1.74	0.810	(311)	
CdS: Al 7.5%(ann.)	450	26.65	3.34	0.960	(111)	11.87
		44.04	2.05	0.870	(220)	
		52.20	1.75	0.880	(311)	

Figure 4 shows the scanning electron microscope of pure and doped CdS by 7.5 vol.% Li and Al thin films of thickness 450±20 nm, grown on ultrasonically cleaned glass substrates at 348 K and annealed to 573 K for 1 h. The images show that the CdS films are best homogeneous surface and less pores after doping with Li and Al. This result is agree with the increase in crystalline sized iagnosed from the results of X-ray diffraction as in Table 2 and 3.

Figure 5 presents AFM two Dimensions (2D) images which allow quantitative measurements of surface features such as Root Mean Square (RMS) or average roughness R_{av} shown in Table 4. From this images, it can be seen that the films are distributed regularly in the form of small granules connected without spaces between them.

Optical properties: The optical transmittance spectra of pure and doped CDs by 2.5, 5, 7.5 vol.% Li and Al thin films of thickness 450±20 nm, grown on ultrasonically cleaned glass substrates at RT and annealed to 573 K for 1 h where investigated using

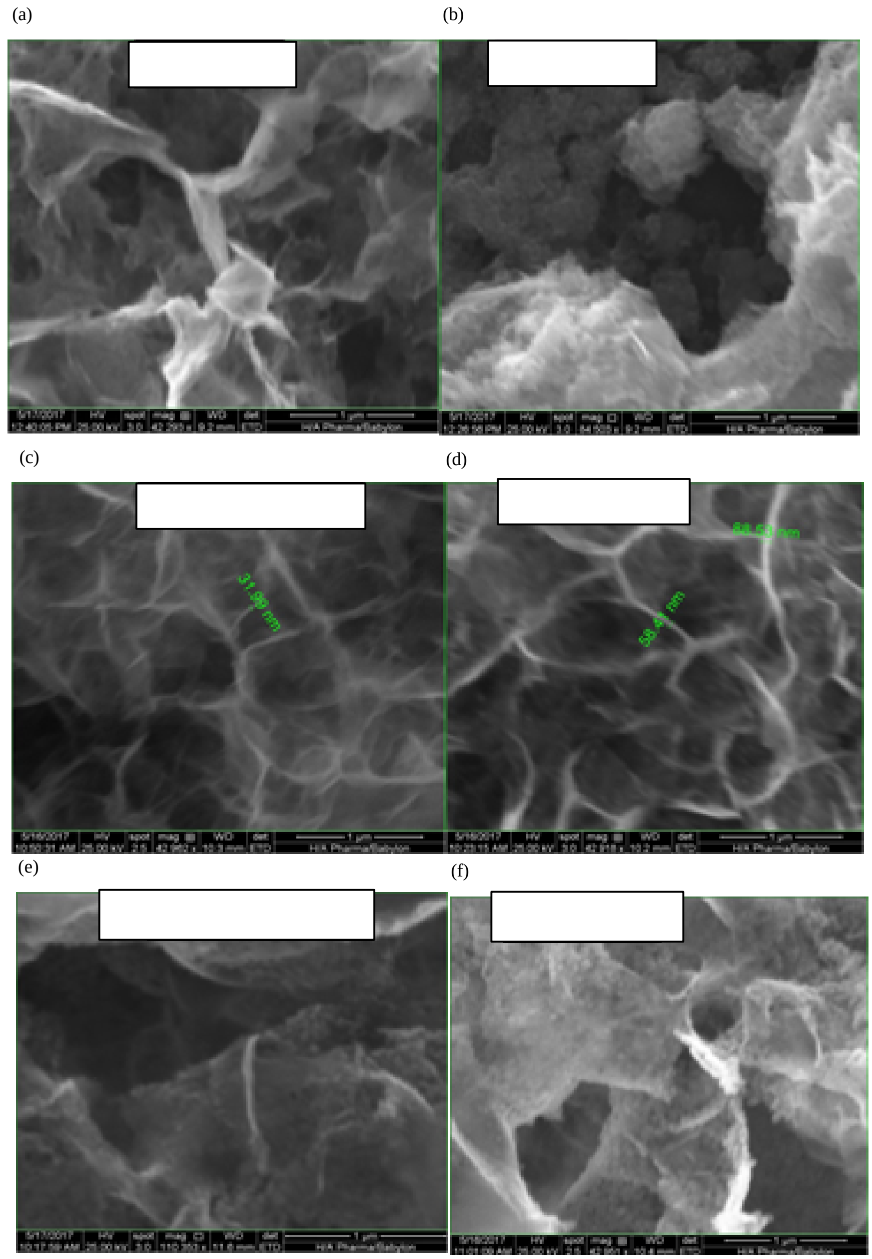

Fig. 4: SEM images of CdS and CdS: 7.5 vol.% Li and Al before and after annealing: a) CdS (ann.); b) CdS; c) CdS: 7.5% Li (ann.); d) 7.5% Li; e) CdS: 7.5% Li (ann.) and f) CdS: 7.5% Al

Table 4: AFM results of CdS and CdS: (2.5, 5, 7.5) vol.% Li and Al

Materials	Root mean square (nm)	Roughness (nm)	Ten point height
CdS	3.37	2.87	7.05
CdS (ann.)	5.61	4.67	14
CdS: 7.5% Li	5.17	4.40	19.5
CdS: 7.5% Li (ann.)	8.36	7.27	15.7
CdS: 7.5% Al	11.4	9.87	39.6
CdS: 7.5% Al (ann.)	7.03	5.98	27.1

UV-visible spectrophotometer in the wavelength ranged from 300-1100 nm as shown in Fig. 6a, b. The results show that the transmittance decrease with increased doping. The sharp increase in transmittance appear at wavelength (500±20) nm followed by a slight increase up to 1100 nm which are in agreement with researches by Sahu and Chandra (1987) and Ravangave *et al.* (2012).

Figure 7a, b show the absorption coefficient as a function of the energy photon (hυ), it can be seen that the films have a high absorption coefficient ($\alpha > 10^4$ cm^{-1}) which indicates direct electronic transitions.

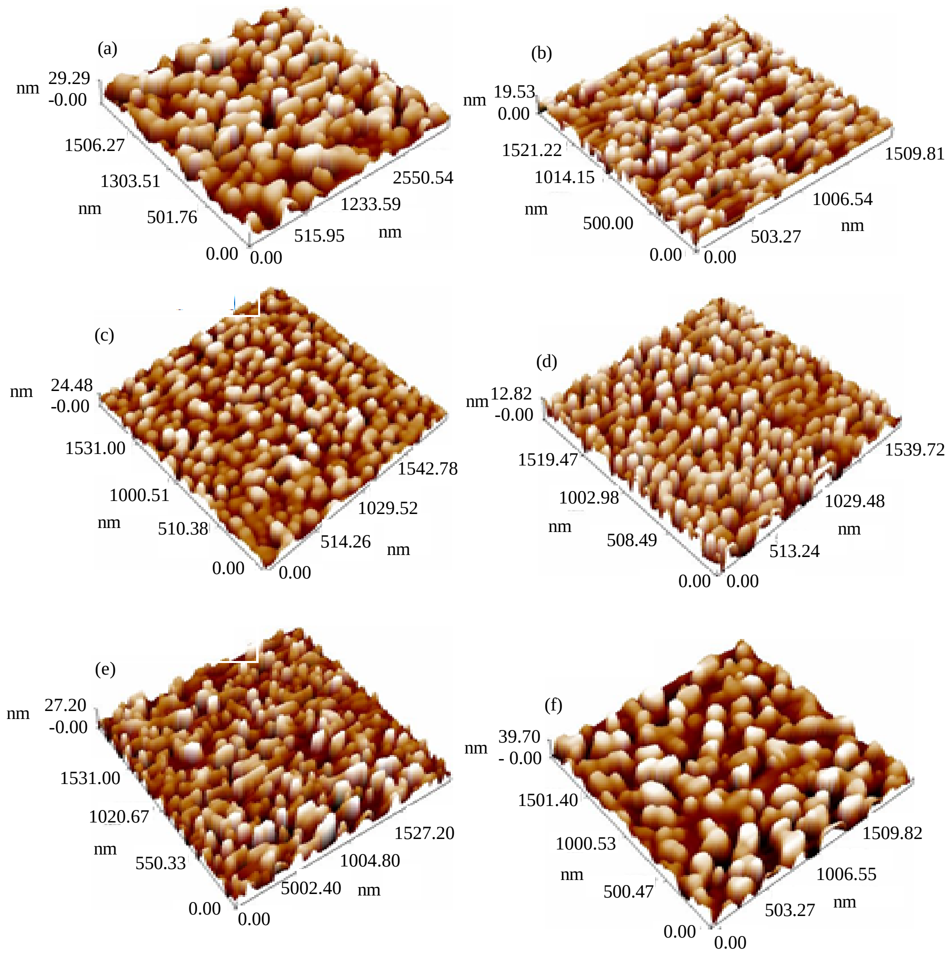

Fig. 5: AFM images of CdS and CDs: 7.5 vol.% Li and Al before and after annealing: a) CdS(ann.); b) CdS; c) CdS: 7.5% Li (ann.); d) 7.5% Li; e) CdS: 7.5% Li (ann.) and f) CdS: 7.5% Al

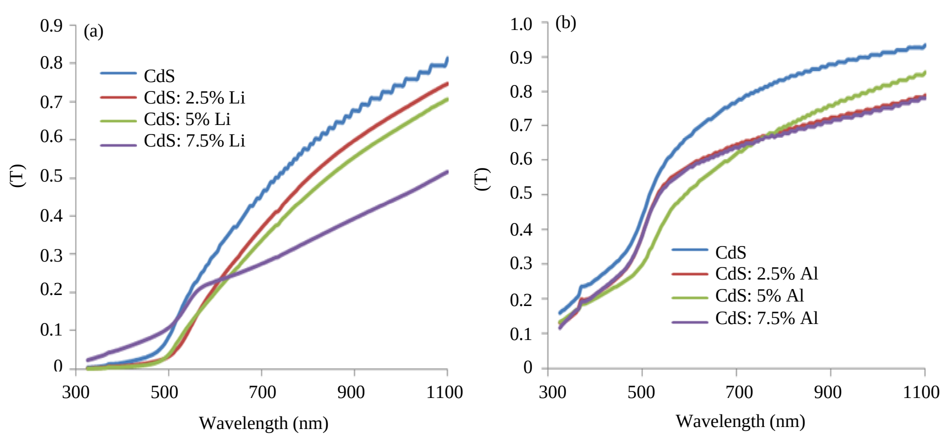

Fig. 6a, b: Optical transmittance of CdS and CDs: (2.5, 5, 7.5) vol.%: a) Li and b) Al for thickness 450 nm

The optical Energy gap (E_g^{opt}) was evaluated by extrapolating the linear part of the curve to the energy axis as in Fig. 8a, b. The allowed direct E_g^{opt} of the (0, 2.5, 5, 7.5) vol% Li and Al doped CDs thin films of thickness 450±20 nm at about (2.89, 2.81, 2.79, 2.72) eV and (2.89, 2.85, 2.79, 2.81) eV, respectively. The higher

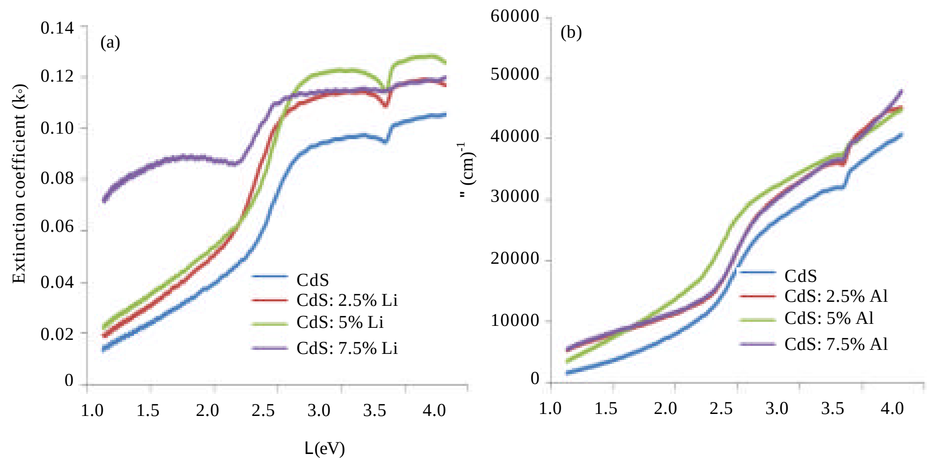

Fig. 7: Absorption coefficientof CdS and CdS: (2.5, 5, 7.5) vol.% a: Li b: Al for thickness 450 nm

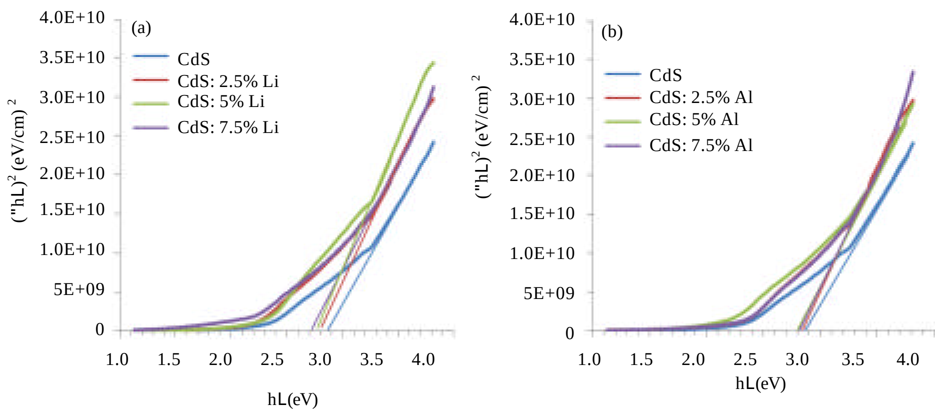

Fig. 8a, b: The optical energy gap for the $(\alpha h\upsilon)^2$ as a function of $(h\upsilon)$ for CdS and CDs: (2.5, 5, 7.5) vol% Li and Al for thickness 450 nm

value of the E_g^{opt} compared with that of the bulk energy gap 2.42 eV indicates the formation of nanostructure and presence of quantum confinement effects in the prepared films (Mousa *et al*., 2011; Das and Pandey, 2011). The decrease in E_g^{opt} may be due to the replacement of larger number of substitutional or interstitial cadmium ions by Li or Al ions, this is because new localized levels have been formed that permeate the fundamental levels (Dhanam *et al*., 2002; Al-Jumaili and Mahmood, 2013).

CONCLUSION

XRD studies of pure and doped CDs by Li and Al thin films before and after annealing indicated the formation of nanocrystalline with polycrystalline hexagonal phase. SEM and AFM imagesindicated that the surface morphology of CdS are best homogeneous and less pores after doping with Li and Al. The high optical transmittance of the films in the Vis-IR regions qualify them features to work as filters and antireflection coating to improve solar cell efficiency. For all films the high absorption coefficient ($\upsilon > 10^4$ cm^{-1}) give indication that the electronic transitions is direct. The optical energy gap decrease with increasing the both doping ratio.

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