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Nanostructures, Stress, Strain And Surface Characterization Of Chemically Synthesized Nano-CrystallineCdSe : Mn^{+2} Ion Thin Films

Ksh. Nandini Devi, H. Jamuna Devi, M. Rasmani Devi, K. Kunjabali Singh
[1] *Department Of Physics, ArunodayaUniversitry, Itanagar-791110,Arunachal Pradesh, India*
[2] *Department Of Physics, South East Manipur (Govt.) College, Komlathabi-795135, Manipur,India*
[3] *Department Of Physics, Thambal Marik (Govt.) College, Oinam-795134,Manipur, India*

Abstract:
CdSe doped with Mn^{+2} ions in the range 1,3,5,7 and 9 at. % thin films were synthesized on to ultrafine ITO substrates by Successive Ionic Layer Adsorption and Reaction (SILAR) technique and studied the nanostructures, micro-strains and stress and dislocation density in the films using XRDand SEM techniques. X-ray diffraction results in the films showed cubic zinc blend structures with preferential reflection along (210)-1at.%, (110)-3at.%, (200)-5, 7 at.% and (110) -9 at.% of Mn^{+2} ion concentrations. The observed lattice parameters a and d – values in the crystal agreed with the standard values. The evaluated particle sizes in the doped CdSe films were found in the nano size regimes and approached quantum dot sizes with increase implantation of Mn^{+2}-ions. The dislocation density, micro-strains and stress in the films were critically studied. The results showed that micro-strains between nano-particles remained almost unchanged, stresses randomized while dislocation density increased with increase of doping dozes in the CdSe nano-crystalline films.
Key words: *CdSe films, XRD, SEM, nanostructures, doping.*

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I. Introduction:

Nano science and nanotechnology are one of the most promising technologies for future civilization. The basic reason is that fabrications and inventions of new devices in thecurrent materialscience and technology world is built on nano-scale size materials. Materials at nano-scale show significantly noble properties entirely different from their bulk counterparts due to high surface area to volume ratio on account of quantum confinement effect[1]. At quantum confinement, materials consist of a large number of very small potential wells in which excitons are trapped and electronic energy levels become discrete. The materials at nano-scale, possess a number of allowed energy states, which under a suitable photo-excitation, can generate unique noble properties. Therefore, the size of the material particles as well as the structural properties of the material play very important roles.The primary work after synthesis of materials is to confirm the crystallinity (*whether crystalline or amorphous)* and to study the structural properties of the material by characterizing it with structural sensitive parameters viz. *(i)crystallinity, (ii) structural phase, (iii) lattice parameters, (v) average grain or particle sizes, (vi) Lattice stress & strains, (vii) lattice defects and (viii) chemical impurity.* These properties immensely influence the mechanical, optical and other electrical and photoelectrical properties of the sample. Attention is, therefore, given to the structural characterization of the grown CdSe doped samples.

Cadmium Selenide with a direct band gap between (1.7-1.8)eV is one of the prominent members of II-VI binary compound semiconductors. The quantum dot is zero dimensional semiconducting nano-crystal whose radius is smaller than the bulk *Bohr exciton radius* of 6nm [2].InCdSe, energy band gap devides the solar spectrum in two parts-(a) thermal part with $hv<E_g$ and (b) optical par with $hv>E_g$[3,4]. Thin films of CdSe polymer nano-composites find potential technological applications in the fabrication of devices like photovoltaic cells, laser, thin film transistors, light emitting diodes, optoelectronic devices and other nanoscale devices[5-7]. Polymer nano-composites are diverse and versatile functional materials in which nano-scale (1-100nm) inorganic particles are dispersed in organic polymer matrix to display enhanced optical, mechanical, magnetic, and opto-electronic properties. Of the three classes of nano-particles, quantum dots which exist nearly in zero dimension is the centre of attraction of the current nano-science research for different technological applications.

II. Experimental Details:

Successive Ionic Layer Adsorptionand Reaction (SILAR) technique was used for synthesis of PVA matrixed equimolar CdSe : Mn^{+2} nanocomposite thin films. In the process, high purity (99.99%) (**AR grade –Aldrish Sigma**) $CdCl_2$ was used as Cd^{+2}-cation source and freshly prepared sodium selenosulphate (Na_2SeSO_3) as Se^{-2}-anion source in presence of trisodium citrate ($Na_3C_6H_5O_7$) as reducing agent.Pure ammonium hydroxide (NH_4OH) was used to adjust the pH of the precursor solution. Polyvinyl alcohol (PVA) matrix was used for controlling the growth and stabilisation of surface morphology of the CdSe thin films. Pure manganese chloride ($MnCl_2$) was used as doping material in the synthesis work at concentrations (1, 3, 5, 7, 9) at. %.

In the process, we prepared 0.4M $CdCl_2$solution by dissolving 8.053 gm of $CdCl_2$ in 100ml de -ionized water. We also prepared 2wt.% PVA solution by dissolving 2gm of PVA in 100ml de-ionized water and the resultant solution was refluxed for 30mins with constant stirring. Now 50ml of $CdCl_2$ solution was mixed with 50ml of PVA solution in a 200ml beaker. Now we prepared 1 at.% Mn^{+2} solution by dissolving 0.071gm of $MnCl_2$ in 5ml DI water. The two precursor solutions were mixed and the entire mixture was stirred for 5mins. The properly cleaned ITO glass substrates (4nos.)were fully immersed vertically in the precursor solution for 8hrs when Cd^{+2}-ions were adsorbed. The substrates were removed and stabilized for 10mins and then gently rinsed with DI water for removal of loose Cd^{+2} –ions.

Preparation of 0.4M sodium solenosulphate (Na_2SeSO_3) solution:

We dissolve 5.04gm of sodium sulphite (Na_2SO_3) at 0.4M in 100ml DI water. Then 0.05mole powder selenium was added to the precursor solution and the resultant mixture was refluxed at 70^0C for 1hr with constant stirring when we obtained 0.4M sodium solenosulphate (Na_2SeSO_3) solution.

Now the substrates were immersed into the precursor solution mixed with 10ml of trisodium citrate and a few drops of NH_4OH solution at pH = 8 for 8hrs when Se^{-2}-ions were adsorbed on the Cd^{+2}-ions pre-deposited substrates. The two opposite ions Cd^{+2} and Se^{-2} –ions reacted to form CdSe doped Mn^{+2} –ions at 1 at.% at 0.4M. The substrates were gently removed, stabilized, rinsed in running DI water, dried in an oven and finally annealed at 50^0C for 24hrs. Similarly we synthesised CdSe thin films doped with Mn^{+2} at doses 3, 5, 7, 9 at.% at 0.4M.

III. Results And Discussion

Structural and morphological characterization:

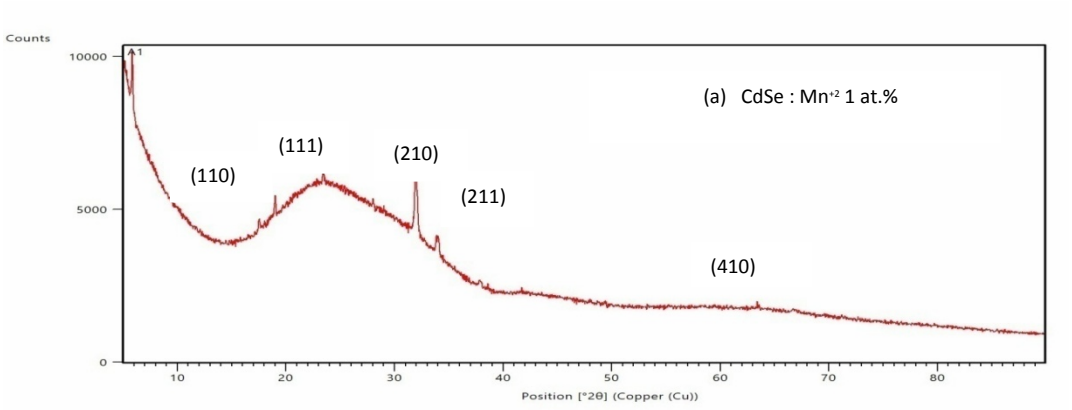
The as synthesized Mn^{+2} –ions doped CdSe thin films at doping implantations 1 at. %, 3 at. %, 5 at. %, 7 at. % and 9 at. % were taken XRDs by low angle X-ray diffractometer (**Phillips X' pert Pro-Automated X-ray model APD 1700**) diffractometer with CuK_α–radiation (λ = 1.572Å) as shown in Figures 1 (a, b, c, d &e) respectively. The XRD-data obtained at different doping concentrations are shown in Table-1.The lattice parameters of the phase structure of the CdSe films at different doping were calculated using Bragg's relation

$$2d\sin\theta = n\lambda \quad (1)$$

whence $$\sin^2\theta = (\lambda^2/4a^2)N \quad (2)$$

where $N = h^2 + k^2 + l^2$ and

$$d_{hkl} = a/\sqrt{(h^2 + k^2 + l^2)} \quad (3)$$



(b) CdSe :Mn^{+2} 3 at.%

(110) – (200)

(210)

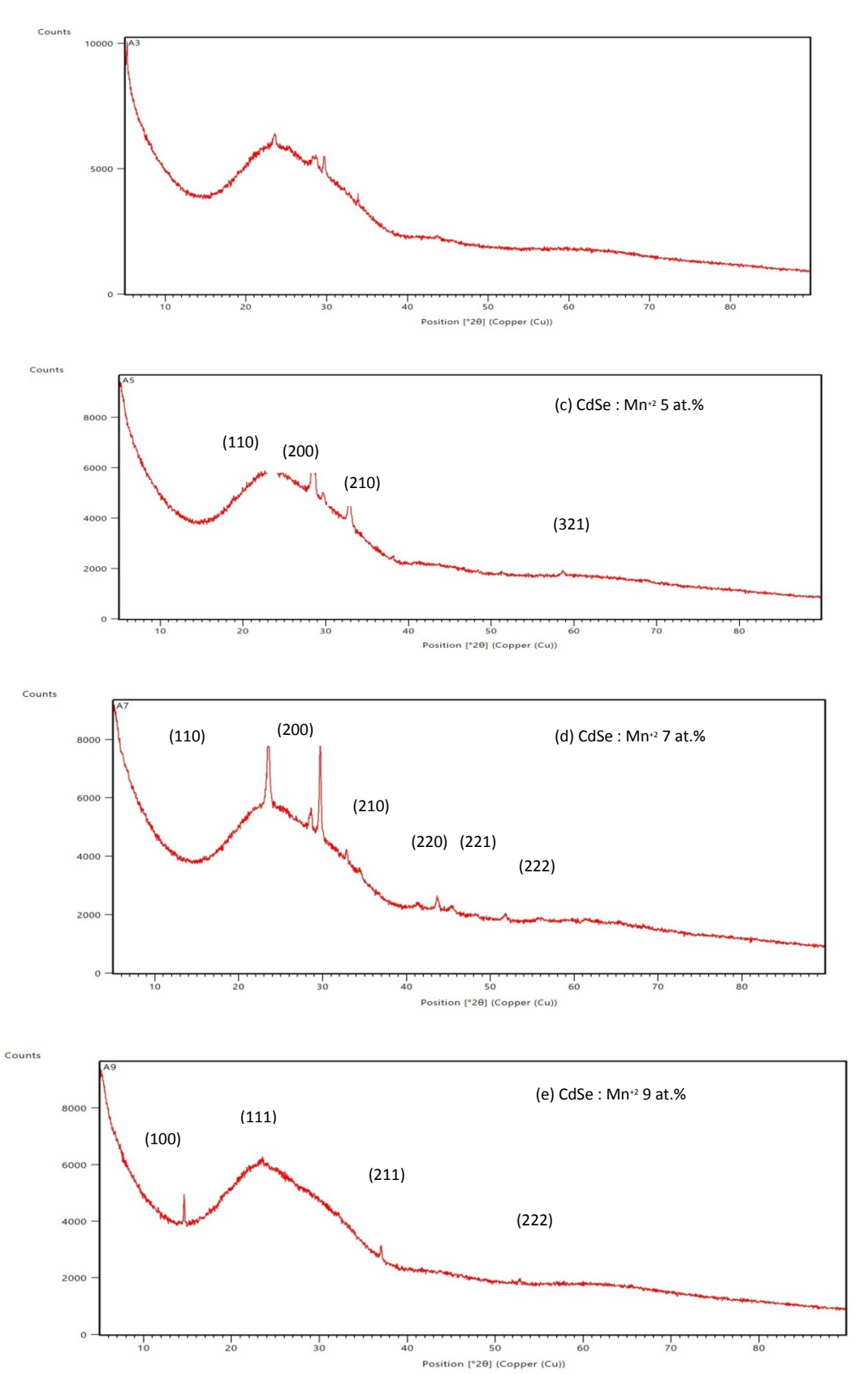


Figure 1. XRD patterns of CdSe thin films doped at different concentrations.

The XRD spectra in the CdSe doped with Mn^{+2} at different doping ranges showed cubic zinc blend structures with preferential reflection along (210)-*1 at.%,* (110)-*3 at.%,* (200)-*5, 7 at.%* and (110) -*9 at.%* as

shown in the Figure1. The (*hkl*) and lattice parameters evaluated of the films are shown in Table-2.It is observed that the evaluated values of lattice parameters *a*-are observed above and below the standard value with increase of low angle X-ray diffraction while *d*-values decrease.This variation in lattice parameters in the doped CdSe films is attributed to lattice strains induced by the formation of oxygen vacancies in the crystal.The SEM surface images of the grown CdSe doped with Mn^{+2} at 1 at. %, 3 at.%, 7 at.% and 9 at. % taken(model **JEOL 1025A)** and are shown in Figure 2 (a, b, c and d) respectively.

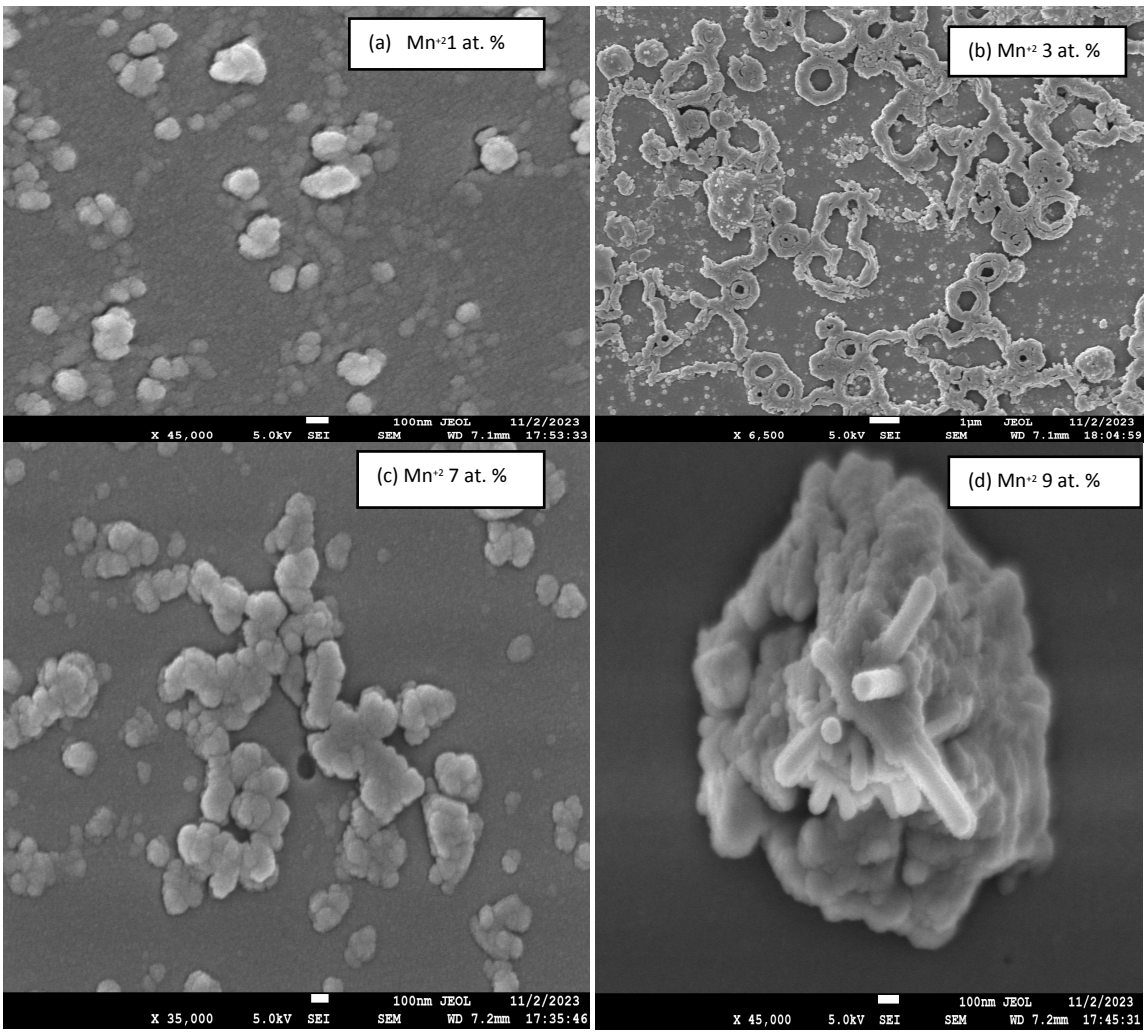


Figure 2. SEM images of surface topology of doped CdSe nanocrystal thin films.

The analysis of SEM-surface topology of the grown CdSe doped films showed that the surface distribution of crystalline particles were uniformly distributed in bubble forms and rode like structures at higher Mn^{+2}-ions concentration in the CdSe films with sizes of particles lying below 100nm.

Table-1. XRD data of CdSe :Mn^{+2} samples.

Mn^{+2} dozes	2θ (degree)	Rel.Int. (%)	Height (cts)	FWHM Left (^{0}2θ)	d-spacing (Å)
1 at.%(CdSe)	5.840	54.56	1937.84	0.1023	15.133
	17.539	26.75	950.23	0.1535	5.056
	19.046	49.42	1755.50	0.1023	4.659
	23.441	80.47	2858.08	0.1535	3.795
	31.955	100.00	3551.92	0.1791	2.800
	34.026	39.74	1411.54	o.2558	2.635
	37.907	6.14	218.26	0.2558	2.373
	63.419	1`2.61	448.02	0.0936	1.465
	66.839	7.03	249.74	0.6140	1.399
3 at.% (CdSe)	5.257	60.73	1870.42	0.1023	16.814
	23.595	100.00	3079.71	0.2558	3.771
	25.340	86.21	2655.12	0.6140	3.515

	28.735	79.45	2446.70	0.2558	3.107
	29.618	81.32	2504.50	0.2303	3.016
	33.878	38.54	1186.92	0.2047	2.645
	43.741	5.22	160.83	0.6140	2.060
5 at.%(CdSe)	23.611	87.58	3093.78	0.3070	3.787
	28.430	100.00	3532.44	0.3582	3.140
	29.696	61.39	2168.65	0.3070	3.008
	32.894	80.34	2837.87	0.2558	2.723
	38.066	4.93	174.26	0.3070	2.364
	51.350	1.83	64.57	0.6140	1.779
	58.677	8.86	312.93	0.4093	1.573
	68.874	5.83	205.91	0.9210	1.363
7 at.%(CdSe)	23.560	98.78	4986.53	0.2303	3.775
	28.629	51.05	2577.39	0.3070	3.118
	29.720	100.00	5048.35	0.2047	3.006
	32.860	29.67	1498.00	0.2047	2.726
	34.500	17.69	893.14	0.3070	2.600
	41.331	3.18	160.60	0.5117	2.185
	43.686	9.28	468.66	0.3070	2.072
	45.389	4.57	230.73	0.5117	1.998
	48.243	1.66	83.89	0.6140	1.886
	51.744	3.76	189.62	0.4093	1.767
	55.894	3.05	154.08	0.8187	1.645
	61.412	5.00	252.62	0.6140	1.510
9 at. % (CdSe)	14.614	37.58	1070.52	0.0768	6.062
	23.387	100.00	2848.71	0.8187	3.804
	37.009	24.79	706.15	0.1023	2.429
	52.766	3.37	95.88	0.3070	1.735

Table-2. Lattice parameters of CdSe : Mn^{+2} ions.

Mn^{+2} dozes	Rel. Int. (%)	2θ (degree)	hkl	JCPDS a-value (Å)	a_{cal}-value (Å)	JCPDS d-value (Å)	d_{cal}-value (Å)
1at.% (CdSe)	26.75	18^0	110	6.050	6.960	5.056	4.923
	49.42	19^0	110		6.597		4.665
	80.47	24^0	111		6.414		3.704
	100.00	32^0	210		6.246		2.993
	39.74	34^0	210		5.889		2.634
	6.14	38^0	211		5.793		2.365
	12.61	64^0	410		5.991		1.453
3at.% (CdSe	100.00	23.5^0	110		5.461		3.862
	86.21	29^0	200		6.151		3.075
	79.45	31^0	200		5.763		2.881
	81.32	34^0	210		5.889		2.634
5at.% (CdSe)	87.58	23^0	110		5.461		3.862
	100.00	28^0	200		6.367		3.183
	61.39	29^0	200		6.151		3.075
	80.34	32^0	210		6.246		2.793
	4.93	58.5^0	321		5.896		1.576
7at.% (CdSe)	98.78	23^0	110		5.461		3.862
	51.05	28^0	200		6.367		3.183
	100.00	30^0	200		5.950		2.975
	29.67	33^0	210		6.062		2.711
	17.69	41^0	220		6.056		2.198
	3.18	44^0	221		6.166		2.055
9at.% (CdSe)	37.58	14^0	100		6.319		6.319
	100.00	24^0	111		6.415		3.704
	24.79	37^0	211		5.943		2.427
	3.37	53^0	222		5.978		1.726

Particle size, dislocation density, micro-strains and stress:

The as grown CdSe :Mn^{+2} films consist of grains of different sizes depending on the doping concentrations**.** The grains or crystallite sizes were calculated using the Scherrer relation [8,9]

$$D_{hkl} = k\lambda/\beta_{2\theta}\cos\theta \quad (4)$$

where the value of the shape factor k is taken as 0.94, $\beta_{2\theta}$, the full width of half maximum intensity (100%) of the sample are taken from the XRD data (Table- 1) and θ the Bragg angle. The values of the grain

sizes at different doping are shown in Table-3. The crystallite sizes of the grown CdSe doped Mn^{+2} - ions are found approaching quantum dot sizes with increasing Mn^{+2} –ion concentrations.

Thechemically synthesized CdSe doped nanocrystalline thin films grown under suitable experimental conditions were observed under various micro-strains on account of some factors like variations of lattice parameters, oxygen vacancies. The micro-strains were calculated using the relation[10]

$$\varepsilon = \beta_{2\theta} [Cot\theta/4] \quad (5)$$

The values of micro-strains are shown in Table-3. The stresses caused by some thermal expansion co-efficient of the films and haphazard grain size orientations were calculated using the relation [11,12]

$$S = E/2\gamma(a_0 - a)/a_0 \quad (6)$$

where $a_0$and a are lattice parameters of CdSe bulk and thin film materials, γ the Poisson ratio taken as 0.37 and E the Young's Elastic Moduli as 42 [13]. The value of a is the average of a_{cal}-values of the films corresponding to sets of Mn^{+2}-ion doping. The dislocation density in the films on account of oxygen vacancies attributed lattice strains were calculated using Willamsonand Smallman's relation[14-16]

$$\delta = 1/D_{hkl}^2 \quad (7)$$

where D_{hkl} is the grain or particle size and are shown in Table-3.

Table-3.Observed grain sizes, dislocation density, micro-strains and stress

Sample (CdSe)	Max. Int. (%)	FWHM Left (^{0}2θ)	Grain size (nm)	Dislocation density (δ) x 10^{14} (lines/m^2)	Micro-strains (ε) x 10^{-2}	Bulk a_0 (Å)	Sample a_{av} (Å)	Stress (GPa)	a_0 from N-R plot (Å)
1 at.%	100	0.1791	46.42	4.64	50.02	6.050	6.270	2.06	6.20
3 at.%		0.2558	32.79	9.30	50.01		5.816	2,20	
5 at.%		0.3582	23.18	18.60	49.98		6.024	0.24	
7 at.%		0.2047	40.57	1.52	50.00		6.523	4.43	
9 at.%		0.8187	10.14	24.29	50.02		6.163	1.06	

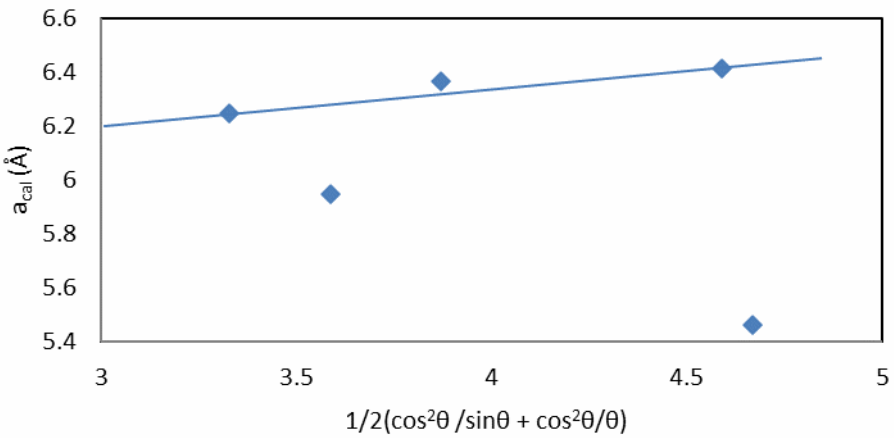


Figure 3. Nelson-Riley plot of the CdSe doped films.

The lattice parameter a_{av} values and a_0 from Nelson-riley plot is shown in Figure 3. The extrapolated a_0 –value is closed agreement with the calculated and standard values as shown in Table-3.

Table-4. Determination of crystal structure

Sample (CdSe)	At intensity 100%				$Sin^2\theta_1/sin^2\theta_2$	$(h_1^2+k_1^2+l_1^2)/h_2^2+k_2^2+l_2^2)$	Cr.struc.
	$(h_1k_1l_1)$	$(h_2k_2l_2)$	Θ_1	Θ_2			
1 at.%	210	211	16^0	19^0	0.72	0.83	f.c.c
3at.%	110	200	11.8^0	14.5^0	0.64	0.50	trans.
5at.%	200	210	14^0	16^0	0.75	0.80	f.c.c
7at.%	200	210	15^0	16.5^0	0.86	0.80	f.c.c
9at.%	111	211	12^0	18.5^0	0.83	0.50	trans.

The as deposited CdSe doped nanocrystals consist of 4 atoms per unit cell with cell dimensions 6.246Å, 5.461Å, 6.367Å, 5.950Å and 6.415Åcorresponding to (210), (110), (200),(200) and (111) planes respectively supporting the f.c.c. cubic zinc sulphide structure. Further, $sin^2\theta_1/sin^2\theta_2$ values corresponding to first

to second reflection planes at maximum intensity of the planes yielded ≥ 0.75 confirms the f.c.c.cubic zinc blend structure[17] as shown in Table-4.

IV. Conclusion

SILAR technique is found to be the easiest method for synthesis of doped or undoped semiconducting thin films from time and economic points of view. The XRD of the as synthesized Mn^{+2}-ions doped thin films in the range of doping concentrations showed exclusively f.c.c. cubic zinc blend structures as confirmed with $\sin^2\theta$ ratio.SEM imaging surface topology in the CdSe films revealed bubble-like uniform distribution of nanoparticles whose sizes range down to 10nm and rode-like at higher doping level.Some localized crystalline dislocation density were observed in the films growing up relatively with increase of Mn^{+2}-ion concentrations. The dislocation density on account of oxygen vacancies attributed micro lattice stress and strains in the chemically synthesized CdSe doped thin films.

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