Characterization of Zinc Doped Cadmium Selenide [$Cd_{1-x}Zn_xSe$] Thin Films Prepared by Vacuum Deposition Technique

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Abstract: The zinc doped cadmium selenide i.e. $Cd_{1-x}Zn_xSe$ is an important semiconducting alloy. the different physical properties can be studied by changing values of x. Thin films of zinc doped cdse ($Cd_{1-x}Zn_xSe$) of a thickness of 1000 Å, 1500 Å, 2000 Å, 2500 Å with different compositions (x = 0.5 and 0.75) were deposited by vacuum deposition technique under the pressure of ~10^{-5} mbar. onto a glass substrate. In this paper, we have studied thin films of a thickness of 2000 Å. The effect of Zinc content on structural, morphological and compositional properties in $Cd_{1-x}Zn_xSe$ thin films has been investigated in the present work. The films showed the dominant hexagonal phase of CdSe and the cubic phase of ZnSe. The lattice parameter a for the hexagonal structure was 4.425 Å, whereas for the cubic structure a is equal to 5.666. The particle size D is nearly equal to 4 Å in a hexagonal and a cubic structure. The XRD pattern shows that the two binary compounds have been completely transformed into a ternary compound with hexagonal (wurtzite) structure and cubic structure and polycrystalline nature. Scanning electron microscopy (SEM) demonstrates the surface morphology of Zinc doped CdSe thin film. The energy dispersive x-ray (EDAX) analysis confirmed the nearly stoichiometric deposition of the film.

Index Terms **-** Thin film, Zinc, Cadmium Selenide, EDAX, Crystal Structure, XRD, Surface Morphology, SEM.

I. INTRODUCTION

The crystallographic structure of zinc doped cadmium selenide i.e ZnxCd1-xSe film is rather sensitive to the preparation conditions. Both cubic or wurtzite structure for all compositions in the range $0 \leq x \leq 1$, as well as the transition from wurtzite in Cd-rich to cubic in Zn rich films, with a mixture of the two phases in between, have been reported [1]. Therefore each effect of the preparation conditions on the crystallographic structure of $Cd_{1-x}Zn_xSe$ films has to be studied carefully. The group II-VI ternary compound semiconductor has a lot of applications in optoelectronics devices ranging from blue to near ultraviolet region [2]. Among them CdSe and ZnSe, which belong to the group II-VI semiconductors are technologically important due to their direct and wide band gap[3]. The $Cd_{1-x}Zn_xSe$ II-VI ternary alloys are direct-gap semiconductors in which the optical band gap variation spans the entire visible range (from 1.75 to 2.7 eV) and the lattice parameter were decreases gradually as the Zn content, x is varied between 0 and 1[4]. The use of polycrystalline Zn doped CdSe thin film has attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices. Due to its excellent optical properties and fast response times Zinc doped Cadmium Selenide [$Cd_{1-x}Zn_xSe$] has a wide range of potential applications in the photoluminescent, electroluminescent, photoconductive and photovoltaic device applications [5, 6]. A number of thin film deposition methods, such as molecular beam epitaxy, electron beam pumping, chemical bath deposition (CBD), etc. have been used for preparing $Cd_{1-x}Zn_xSe$ thin films [7– 9]. We have prepared $Cd_{1-x}Zn_xSe$ films by the vacuum deposition technique with the various zinc content. $Cd_{1-x}Zn_xSe$ thin films have been studied by many researchers [10–12], but the effect thickness on physical properties of $Cd_{1-x}Zn_xSe$ thin films is rarely presented in the literature. In the present work, thin films of $Cd_{1-x}Zn_xSe$ are deposited on glass substrates by the vacuum deposition technique [1, 7]. The deposited films are characterized using X-ray diffraction, Scanning electron microscopy and Energy dispersive analysis by X-rays. The effect of the proportion of zinc on structural, morphological, compositional and optical properties of the films are studied and the results are discussed [8].

II. EXPERIMENTAL

(A)Thin Film Deposition

The glass slides were washed in a detergent soap solution, distilled water and acetone one by one to remove the impurities from their surfaces. The cleaned glass slides were dried and then used for thin film deposition in a Hind High Vac vacuum unit[1, 7]. Thin films of Zn doped CdSe were deposited by vacuum deposition technique at the vacuum of ~10^{-5} Torr. By the rotary pump and diffusion pump. The vacuum deposition unit has two pressure gauges, Pirani Gauge for measuring low vacuum up to 10^{-3} Torr and a very sensitive Penning Ionization Gauge which measures a relatively high vacuum from 10^{-2} to 10^{-5} Torr [7]. The source material Zn doped CdSe [$Cd_{1-x}Zn_xSe$] is in ingot form, a compound of Zn doped CdSe [$Cd_{1-x}Zn_xSe$] is obtained by mixing granule of pure zinc material with granules of pure cadmium and pure selenium powder in an equal ratio of their atomic weight at a very high temperature in a quartz glass tube. here the materials are used of Sigma Aldrich chemical company having a purity of 99.99 %[7-9]. The uniformly mixed compound of Zn doped CdSe [$Cd_{1-x}Zn_xSe$] was grounded in powdered form and it was placed in a molybdenum boat for evaporation. The glass substrate was placed above the source at a fixed distance. The deposition rate was maintained (02 - 06 Å/sec) throughout the thin film preparation[13-14]. The source temperature varies from 700 ^{0}C to 1100 ^{0}C at which source material start evaporation. The substrates temperature were kept at constant by a continuous flow of cold water from a tap. The films of Zn doped CdSe [$Cd_{1-x}Zn_xSe$] of thicknesses 1000 Å, 1500 Å, 2000 Å, and 2500 Å were deposited under the almost same environment. The thickness monitor model no. DTM - 101 provided by Hind-High Vac using which the different thickness of thin films was monitored [7, 15]. The different preparation parameters have been varied and optimized for uniform deposition of thin films. The vacuum deposited thin films were found to be uniform, porous free and adhered well with the glass slides. The lattice spacing (d), The lattice parameter (a) and The particle size (D) was calculated [16].

B) *Characteristics*

The X-ray diffraction (XRD) was used to investigate the structure of Zn doped CdSe [$Cd_{1-x}Zn_xSe$] thin films of thickness 2000 Å. The particle size (D) is calculated from the full width at half maximum β (FWHM) using the Scherer's formula [17].

$$D = 0.94\lambda / \beta \cos \Theta$$

Where D is the mean dimension of the crystallites, Θ is the Bragg's angle and λ the wavelength of X-ray
The lattice parameter (a) for the hexagonal and cubic structure is determined by using the following expression[7].

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$$

The interplanar spacing '*d*' in the crystal has been determined By applying Bragg's law using the X-rays of known wavelength and measuring the angle of diffraction 2 θ of the most intense peak[18]. The structure of the films was evaluated by X-ray diffractometer using nickel filtered copper Kα radiation with wavelength λ=1.54060 Å, the formula is given as,

$$n\lambda = 2d \sin \theta$$

where '*d*' is lattice spacing, '*θ*' is the angle between the incident beam and the planes (hkl), '*λ*' is a wavelength of monochromatic X-rays, '*n*' is the order of reflection (n = 1, 2, 3,…..)[10, 14].
SEM is the most suitable technique for the topography and Surface morphological study of the Zn doped CdSe [$Cd_{1-x}Zn_xSe$] thin film. SEM gives valuable information regarding the growth mechanism, shape and size of the particles and/or grains in the films [13]. The EDAX is used for studying the chemical composition of the sample.

III. RESULTS AND DISCUSSIONS

Structural analysis of the Zn doped CdSe thin films of 2000 Å thickness is carried out by XRD technique Cu Kα radiation (l =1.54060 Å). using Bragg's equation 'd' value calculated for the known value of θ, λ, and n. The hkl indices are obtained by comparing the XRD data of deposited Zn doped CdSe thin films with the Joint Committee on Powder Diffraction Standard (JCPDS) data cards [1,7,10]. Scan angle with angular range $05° \leq 2\theta \leq 80°$ at 40 kV voltage and 40 mA current. using the Scherer's formula the particle size (D) is calculated from the full width at half maximum β (FWHM). Where β is equal to 0.406 [1,7]. Due to a larger atomic radius of Cd in comparison with the Zn atomic radius, the decrease of the Zn content causes a shift of this peak to the higher 2θ angles in respect to its position in the spectrum of pure CdSe (for which x = 0). The substitution of Cd with Zn atoms leads to a decrease of the lattice parameter "a" [19]. The bands in the CdSe spectrum are typical for wurtzite structure of CdSe of crystallographic planes{100} at 23.900º, {101} at 27.080º, {102} at 35.090º, {110} at 41.960^0 , and {103} at 45.770º (JCPDS 08-0459). On the other hand, the bands in the ZnSe spectrum are typical for cubic structure. the peaks at 27.230º, 45.200º, 53.600º , and 65.840º are due to X-ray diffraction from the {111}, {220} {311} and {400} families of crystallographic planes (JCPDS 19 - 0191) [20]. The formation of cubic structure in $Cd_{1-x}Zn_xSe$ films with $x = 0.75$ has been reported, while films with $x = 0.5$ have shown a hexagonal wurtzite structure. The Zn doped CdSe thin films changes in the film structure from hexagonal in Cd-rich to cubic in Zn-rich films, single cubic, and wurtzite structure have also been reported [12].
The XRD patterns of crystalline Zn doped CdSe [$Cd_{1-x}Zn_xSe$] thin film is shown in Figure 1 and 2

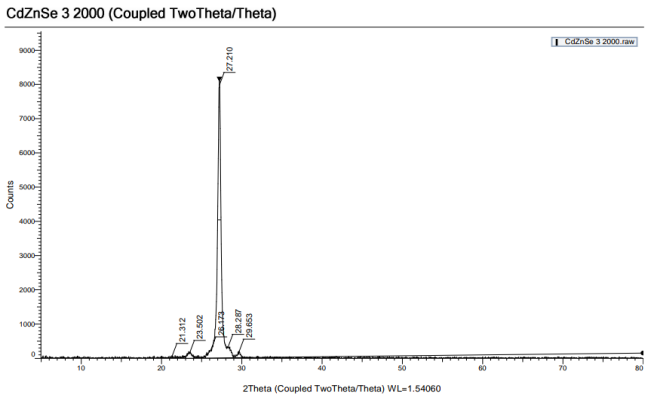


Fig. 1: XRD of **$Cd_{0.5}$ $Zn_{0.5}$Se** films of thickness 2000 Å

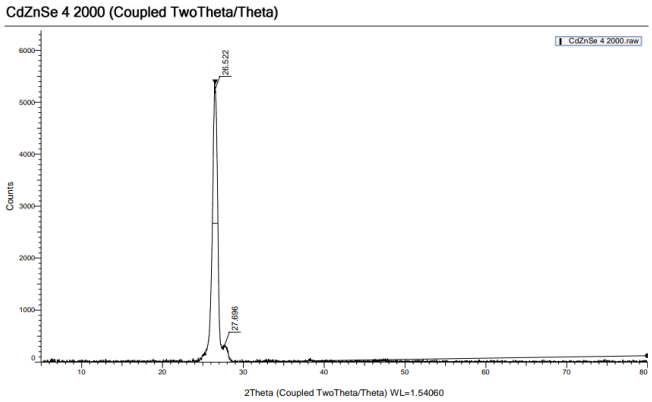


Fig. 2: XRD of **$Cd_{0.25}$ $Zn_{0.75}$Se** films of thickness 2000 Å

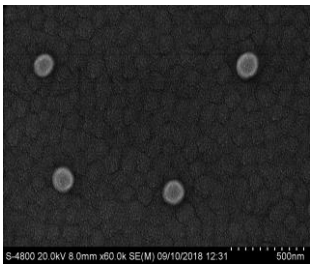
Table 1. X-ray diffractogram (XRD) JCPDS hexagonal data for **$Cd_{0.5}$ $Zn_{0.5}Se$** and **$Cd_{0.25}$ $Zn_{0.75}Se$** sample of thickness 2000 A^0

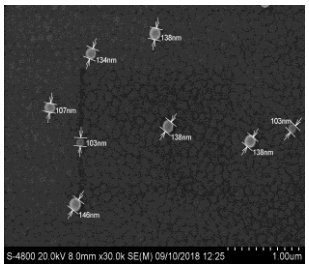
[hkl] values from JCPDS data	d(Å) values from JCPDS data of cdse	Observed values of d(Å) **$Cd_{0.5}$ $Zn_{0.5}Se$**	Observed (2ɵ)° values of peaks	intensity	Observed values of d(Å) **$Cd_{0.25}Zn_{0.75}Se$**	Observed (2ɵ)° values of peaks	intensity	Lattice parameter a(Å)	Particle size D (Å)
100	3.720	3.720	23.900	595	3.720	23.900	434	3.724	3.645
002	3.510	3.509	25.370	646	3.509	25.370	661	4.972	3.655
101	3.290	3.290	27.080	6433	3.290	27.080	1081	4.652	3.668
102	2.554	2.555	35.090	325	2.555	35.090	257	5.713	3.740
110	2.151	2.151	41.960	264	2.151	41.960	204	3.041	3.820
103	1.980	1.980	45.770	234	1.980	45.770	245	6.261	3.871
200	1.863	1.863	48.830	234	1.863	48.830	247	3.722	3.917
112	1.834	1.834	49.670	184	1.834	49.670	207	4.492	3.930
201	1.800	1.800	50.660	222	1.800	50.660	176	4.024	3.946
202	1.645	1.645	55.820	199	1.645	55.820	174	4.652	4.036
203	1.456	1.457	63.830	199	1.457	63.830	159	5.249	4.202
210	1.407	1.406	66.440	189	1.406	66.440	144	3.146	4.263
211	1.380	1.380	67.820	208	1.380	67.820	128	3.338	4.297
105	1.312	1.311	71.960	144	1.311	71.960	129	6.668	4.407
212	1.305	1.305	72.350	154	1.305	72.350	161	3.915	4.418
300	1.241	1.239	76.820	117	1.239	76.820	139	3.723	4.552
301	1.221	1.221	78.170	152	1.221	78.170	147	3.861	4.595
213	1.205	1.204	79.520	143	1.204	79.520	127	4.508	4.639

Table 2. X-ray diffractogram (XRD) JCPDS cubic data for **$Cd_{0.5}$ $Zn_{0.5}Se$** and **$Cd_{0.25}$ $Zn_{0.75}Se$** sample of thickness 2000 A^0

[hkl] values from JCPDS data	d(Å) values from JCPDS data of znse	Observed values of d(Å) **$Cd_{0.5}Zn_{0.5}Se$**	Observed (2ɵ)° values of peaks	intensity	Observed values of d(Å) **$Cd_{0.25}Zn_{0.75}Se$**	Observed (2ɵ)° values of peaks	intensity	Lattice parameter a(Å)	Particle size D (Å)
111	3.273	3.273	27.230	8675	3.273	27.230	772	5.669	3.670
200	2.835	2.836	31.520	440	2.836	31.520	341	5.670	3.706
220	2.004	2.005	45.200	265	2.005	45.200	235	5.670	3.863
311	1.707	1.708	53.600	235	1.708	53.600	175	5.661	3.996
222	1.635	1.635	56.150	180	1.635	56.150	160	5.663	4.042
400	1.417	1.417	65.840	193	1.417	65.840	157	5.668	4.249
331	1.300	1.300	72.650	152	1.300	72.650	146	5.666	4.427
420	1.267	1.267	74.832	158	1.267	74.832	130	5.666	4.490

For the topography study of sample, SEM is a promising technique, as it provides us valuable information regarding the growth mechanism, shape and size of the particles and/or grains in thin films[11-13]. The SEM pictures of $Cd_{0.5}Zn_{0.5}Se$ and $Cd_{0.25}Zn_{0.75}Se$ thin films of thickness 2000 Å deposited on a glass substrates are shown in Figure 3 and 4. The Surface morphology by SEM image of the deposited film reveals the well adhesive uniform surface nature on glass substrate. as well as very small, fine and hardly distinguishable grains smeared all over the surface[14-17]. No crack was observed on the surface of the Zn doped CdSe thin films. The spherical and flower-like shape of the particles can be observed easily in high magnification micrographs[18]. SEM observations show the crystalline growth for the deposited Zn doped CdSe thin films [19]. The present work, SEM investigations are done by using an SEM instrument at K.B.C.N.M.U., Jalgaon


(a)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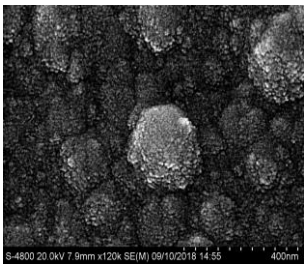
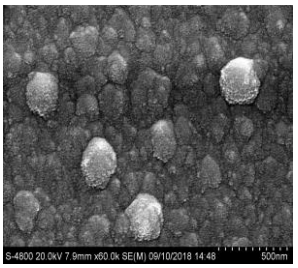

(i)


(ii)

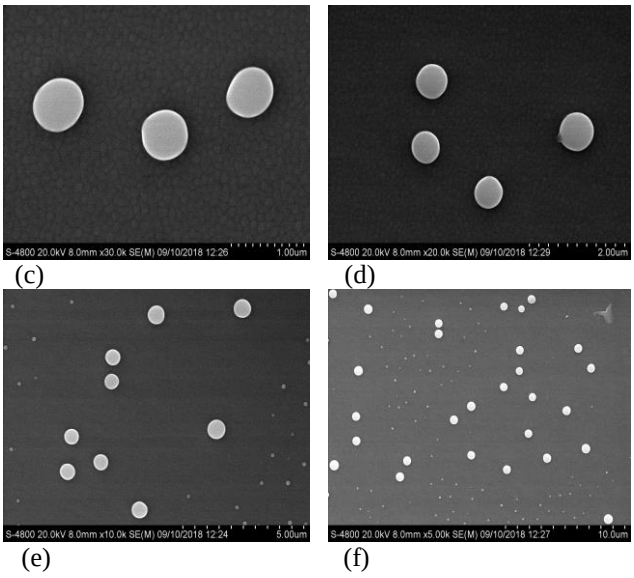


Figure 3 : SEM pictures taken for **$Cd_{0.5}$ $Zn_{0.5}Se$** films with different x content
(a) 500 nm, x = 60k (b) 1 µm, x = 30k (c) 1.0 µm, x = 30k
(d) 2.0 µm, x = 20k (e) 5.0 µm, x = 10k (f) 10 µm, x = 5k

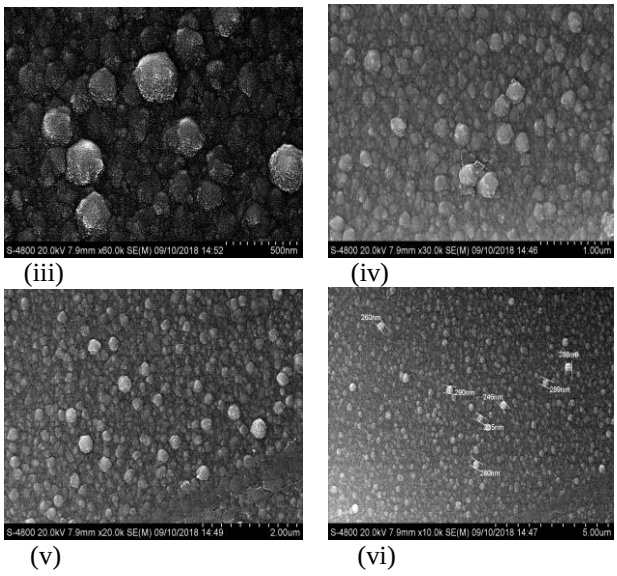


Figure 4 : SEM pictures taken for **$Cd_{0.25}$ $Zn_{0.75}Se$** films with different x content
(i) 400 nm, x = 120k (ii) 500 nm, x = 60k (iii) 500 nm, x = 60k
(iv) 1.0 µm, x = 30k (v) 2.0 µm, x = 20k (vi) 5.0 µm, x = 10k

The presence of elemental constituents in Zn doped CdSe thin film is confirmed from EDAX analysis[20]. The films were deposited on glass substrates It is found that the films are showing Cd and Zn content less than the percentage present in the starting material. However, the selenium content is always present in stoichiometric percentage and deficient[12-15]. These results show the *n*-type nature of these Zn doped CdSe thin films as Se is present in more proportion [16-18].

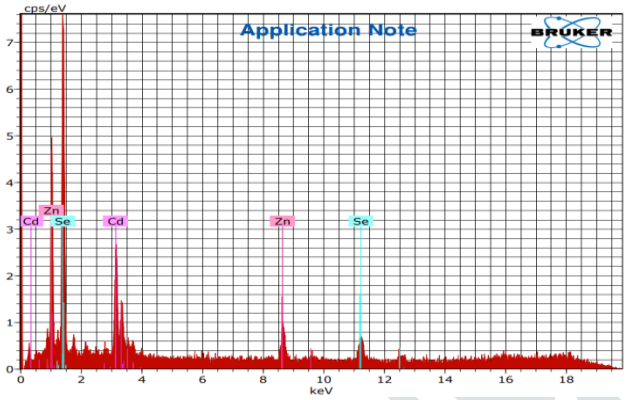


Fig 5 :- EDAX spectra of **$Cd_{0.5}$ $Zn_{0.5}Se$**

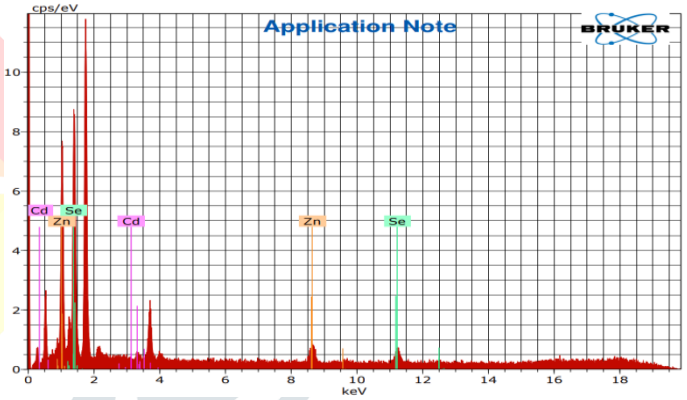


Fig 6 :- EDAX spectra of **$Cd_{0.25}$ $Zn_{0.75}Se$**

Table 3 EDAX mass and atomic percentage of Zn, Se and Cd

Element		$Cd_{0.5}$ $Zn_{0.5}Se$		$Cd_{0.25}$ $Zn_{0.75}Se$	
		Mass %	Atomic %	Mass %	Atomic %
Zn	30	15.57	20.41	22.04	25.69
Se	34	47.07	51.10	74.71	72.11
Cd	48	37.36	28.49	3.25	2.20

IV. CONCLUSION

From XRD It is found that the deposited Zn doped CdSe films of thickness 2000 Å show wurtzite structure along crystallographic planes (100),(101),(102),(110) and (103) and for cubic structure the preferred crystal orientation is along (111), (220),(311) and (400) planes. The X-ray diffraction analysis clearly shows that films are polycrystalline in nature. The lattice parameters are almost matching with the JCPDS data of CdSe and ZnSe. The values of lattice constant 'a' are 4.425 Å and 5.666 Å and the average particle size D = 4.088 Å and 4.055 Å for wurtzite and cubic structure respectively.
The SEM shows uniform growth of Zn doped CdSe films on a glass substrate. The particles are spherical and flower-like in shape. The results of SEM shows that the sizes of grain were from 103 nm to 146 nm for $Cd_{0.5}$ $Zn_{0.5}Se$ thin films and 235 nm to 290 nm for $Cd_{0.25}$ $Zn_{0.75}Se$ thin films.
The presence of elemental constituents is confirmed from EDAX analysis. Strong peaks for Cd and Se were found in the spectrum of $Cd_{0.5}$ $Zn_{0.5}Se$. While strong peaks for Zn and Se were found in the spectrum of $Cd_{0.25}$ $Zn_{0.75}Se$.

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