

Study of Properties of Vacuum Deposited ZnCdSe Thin Films

¹Premjeet G. Jadhav,²Deelip S. Bhavsar

¹Assist. Professor (Research Student),²Associate Professor(Guide)

¹Department of Physics, M.J. College Jalgaon, K.B.C.N.M.U. Jalgaon, India,

¹Department of Electronics, Pratap College Amalner, K.B.C.N.M.U. Jalgaon, India.

Abstract: This research is based on an important semiconducting alloy i.e. zinc doped cadmium selenide $Zn_xCd_{1-x}Se$ ($x = 0.5$ and $x = 0.75$). Thin films of zinc doped cdse ($Zn_xCd_{1-x}Se$) with different composition of x of a thickness of 1000 Å, 1500 Å, 2000 Å, 2500 Å were deposited by vacuum deposition technique under the high pressure of $\sim 10^{-5}$ mbar onto a glass substrate. Core materials of zinc, cadmium and selenium of sigma eldritch of very high purity have been used for thin film deposition. In this work, we have studied zinc doped cdse ($Zn_{0.75}Cd_{0.25}Se$) thin films of a thickness of 1500 Å. The effect of Zinc content on different physics and chemical properties in $Zn_{0.75}Cd_{0.25}Se$ thin films has been investigated. The XRD pattern shows that the two binary compounds have been completely transformed into a ternary compound with hexagonal and cubic structure and thin films are polycrystalline in nature. Scanning electron microscopy (SEM) gives details of the surface morphology of Zinc doped CdSe thin film. The energy dispersive x-ray (EDAX) analysis gives an elemental composition of materials of the thin film. Atomic Force Microscopy (AFM) provides a three-dimensional surface profile of the thin film. The Fourier Transform Infrared Spectroscopy (FTIR) analysis method uses infrared light to scan thin films and observe chemical properties.

Index Terms - Thin film, ZnCdSe, EDAX, XRD, Surface Morphology, SEM, AFM, FTIR.

I. INTRODUCTION

The Coupling of cadmium selenide and zinc selenide would produce a material like ZnCdSe with various band gap energies depending upon the composition of mixture. ZnCdSe will be suitable for increased absorption of solar spectrum and may enhanced resistance towards photo corrosion [5]. Zinc Cadmium Selenide ($Zn_xCd_{1-x}Se$), is one of the ternary alloys of II-VI group, plays an important part in the modern material science and technology. ZnCdSe is an n-type semiconductor material having wide optical band gap from 1.75 to 2.7 eV [2,9]. The lattice parameter in $Zn_xCd_{1-x}Se$ were decreases gradually as the Zn content, x is varied between 0 and 1[7]. Both the CdSe and the ZnSe compounds are known to exist in either cubic zinc blende or hexagonal wurtzite crystal forms depending on the conditions of preparation and the composition [2,8]. The use of polycrystalline Zn doped CdSe ($Zn_xCd_{1-x}Se$), thin film has attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices like laser screen materials in projection color TV's ,nuclear radiation detectors, light emitting diodes, laser diodes. Due to its optical properties, electrical properties and fast response times Zinc doped Cadmium Selenide [$Zn_xCd_{1-x}Se$] thin films has a wide range of potential applications in the photo luminescent, electroluminescent, photoconductive and photovoltaic device applications [10,12]. A number of thin film deposition methods, such as Molecular Beam Epitaxy, Electron Beam Pumping, Chemical Bath Deposition (CBD), Electro Deposition, Ion Sputtering and Vacuum Deposition etc. have been used for preparing $Zn_xCd_{1-x}Se$ thin films [9]. Among the above mentioned deposition techniques, vacuum deposition technique is most attracting and convenient technique due to its remarkable ability to produce thin films with comparable quality to those thin films which are produced by other expensive and sophisticated deposition techniques[7].We have prepared $Zn_xCd_{1-x}Se$ films by the vacuum deposition technique with the various zinc content like $Zn_{0.75}Cd_{0.25}Se$. The $Zn_xCd_{1-x}Se$ thin films have been studied by very few researchers, but the effect of thickness on physical, chemical, electrical and optical properties of $Zn_xCd_{1-x}Se$ thin films is rarely presented in the literatures[4]. In the present work, thin films of $Zn_{0.75}Cd_{0.25}Se$ are deposited on glass substrates by the vacuum deposition technique. The deposited films are characterized using XRD, SEM, EDAX, FTIR & AFM and the effect of the proportion of zinc on structural, morphological, compositional and optical properties of the $Zn_{0.75}Cd_{0.25}Se$ films are studied and the results are discussed [2].

II. EXPERIMENTAL

(A)Thin Film Deposition

Thin films of Zn doped CdSe i.e. $Zn_{0.75}Cd_{0.25}Se$ was deposited by vacuum deposition technique by achieving vacuum up to 10^{-6} torr with the help of the rotary pump and the diffusion pump[1]. The vacuum deposition unit has pressure and Pirani Gauges for measuring low vacuum up to 10^{-3} torr and a Penning Gauge which measures a relatively high vacuum from 10^{-2} to 10^{-6} torr [2]. The glass slides which were used as a substrate were washed to remove the impurities from their surfaces. The cleaned non conducting glass slides were dried and then used for $Zn_{0.75}Cd_{0.25}Se$ thin film deposition in a Hind High Vac vacuum unit [1, 7]. The source material for $Zn_{0.75}Cd_{0.25}Se$ thin film is in ingot form, this compound of Zn doped CdSe [$Zn_{0.75}Cd_{0.25}Se$] is obtained by mixing of granule of pure zinc material, pure cadmium granules and powder of pure selenium in an equal ratio of their atomic weight at a high temperature in a quartz tube. Here the materials of a purity of 99.999 % of Sigma Aldrich were used [5-8]. The compound formed by uniform mixing of zinc, cadmium and selenium [$Zn_{0.75}Cd_{0.25}Se$] was grounded in powdered form in porcelain dish and then it was placed in a molybdenum boat for evaporation. The glass substrate was fixed above the source at a fixed distance in vacuum dome. The deposition rate was maintained (02 - 06 Å/sec) throughout the preparation of $Zn_{0.75}Cd_{0.25}Se$ thin film [13-14]. The source temperature varies from 600 °C to 1200 °C at which source material start evaporation. The substrates temperature was kept at constant and at a lower rate by a continuous circulation of cold water from a tap. The films of Zn doped CdSe [$Zn_{0.75}Cd_{0.25}Se$] of various thicknesses were deposited under the almost same environment and monitored by digital thickness monitor of Hind-High Vac machine [2, 5]. By varying and optimizing the different preparation parameters, a

uniform, porous free and well adhere thin films on glass slides are deposited. The Dislocation density (δ), lattice spacing (d), the lattice parameter (a), the particle size (D) and Micro strain (ϵ_s) was calculated. [10,14].

B) Characteristics –

The structural investigation of $Zn_{0.75}Cd_{0.25}Se$ thin film of thickness 1500 \AA has been carried out by The X-ray diffraction (XRD). The particle size (D) is calculated by using The Scherer's formula [1,2]

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

Where λ the wavelength of X-ray, Θ is the Bragg's angle and D is the mean dimension of the crystallites.

The lattice parameter (a) for the thin film is determined by using the following expression [6,14].

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

The interplanar spacing ' d ' has been obtained by using Bragg's law [18]. The structure of the $Zn_{0.75}Cd_{0.25}Se$ film was evaluated by X-ray diffractometer using nickel filtered copper $K\alpha$ radiation having wavelength $\lambda=1.54060 \text{ \AA}$, the formula is given as,

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

Where ' λ ' is a wavelength of monochromatic X-rays, ' θ ' is the angle between the incident beam and the planes (hkl), ' d ' is lattice spacing, ' n ' is the order of reflection ($n = 1, 2, 3, \dots$)[10,15].

Dislocation density is calculated by using formula $\delta = \frac{1}{D^2}$

Micro strain of given thin film is also obtain by formula $\epsilon_s = \frac{\beta \cos \theta}{4}$ (11)

Surface morphological and topographical study of the $Zn_{0.75}Cd_{0.25}Se$ thin film is done by SEM. The SEM gives accurate information regarding the growth mechanism, shape and size of the particles in the films [8]. The chemical composition of the materials of thin film is studied by the EDAX. The FTIR analysis method uses infrared light to study the chemical properties of the materials used in $Zn_{0.75}Cd_{0.25}Se$ thin film. The 2D and 3D surface structural and morphological properties have been studied by using AFM technique [8,10].

III. RESULTS AND DISCUSSIONS

X – Ray Diffraction - Structural analysis of the $Zn_{0.75}Cd_{0.25}Se$ thin films of thickness 1500 \AA is carried out by XRD technique at $Cu K\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$). Using Bragg's formula the ' d ' value calculated for the known value of θ , λ , and n . The hkl indices are obtained by comparing the XRD data of deposited $Zn_{0.75}Cd_{0.25}Se$ thin films with the Joint Committee on Powder Diffraction Standard (JCPDS) data [1, 8,10]. Scan angle i.e. 2θ with angular range 05° to 80° is used at 40 kV voltages and 40 mA current. The Scherer's formula is used to calculate the particle size (D) from the β (FWHM) which is equal to 0.615 [1,11]. Due to a larger atomic radius of Cadmium in comparison with the Zinc, the decrease of the Zinc content causes a shift of this XRD peak to the higher 2θ angles in the spectrum of pure CdSe (for which $x = 0$). Due to the substitution of Cadmium with Zinc atoms leads to a decrease of the lattice parameter " a " [19]. The bands in the CdSe XRD spectrum are typical for wurtzite structure of crystallographic planes $\{100\}$ at 23.900° , $\{002\}$ at 25.370° , $\{101\}$ at 27.080° , $\{102\}$ at 35.090° , $\{110\}$ at 41.960° , and $\{103\}$ at 45.770° (JCPDS 08-0459). On the other hand, the bands in XRD of the ZnSe spectrum are typical for cubic structure. The peaks at 27.230° , 31.520° , 45.200° , 53.600° , and 65.840° are due to X-ray diffraction from the $\{111\}$, $\{200\}$, $\{220\}$ $\{311\}$ and $\{400\}$ families of crystallographic planes (JCPDS 19 - 0191) [2]. The formation of a cubic as well as a hexagonal wurtzite structure in $Zn_{0.75}Cd_{0.25}Se$ films has been reported. The Zn doped CdSe ($Zn_{0.75}Cd_{0.25}Se$) thin films changes in the film structure from hexagonal in Cd-rich to cubic in Zn-rich films, single wurtzite and cubic structure have also been reported in this study[12,15].

The XRD patterns of crystalline Zn doped CdSe [$Zn_{0.75}Cd_{0.25}Se$] thin film is shown in Figure 1 and 2

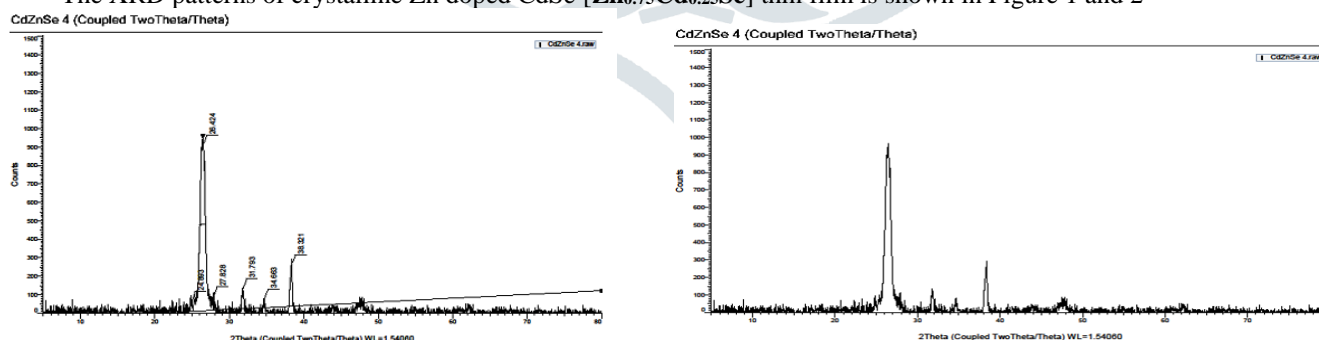


Fig. 1 & 2: XRD of $Zn_{0.75}Cd_{0.25}Se$ films of thickness 1500 \AA

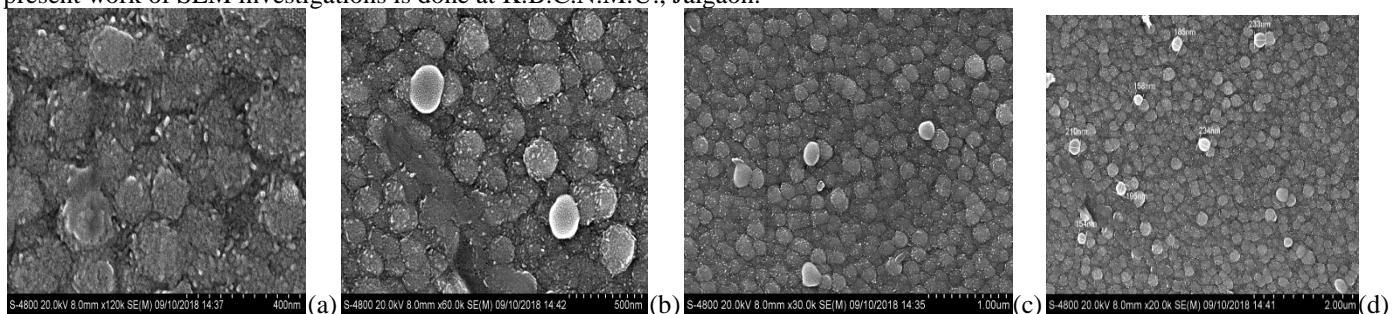
Table 1. X-ray diffractogram (XRD) JCPDS hexagonal data for $Zn_{0.75}Cd_{0.25}Se$ sample of thickness 1500 Å⁰

[hkl] values from JCPDS data	d(Å) values from JCPDS data of cdse	Observed values of d(Å) $Zn_{0.75}Cd_{0.25}Se$	Observed $(2\theta)^{\circ}$ values of peaks	intensity	Lattice parameter a(Å)	Particle size D (Å)	Dislocation density δ ($\times 10^{15}$ lines/m ²)	Micro strain (ϵ_s)
100	3.720	3.720	23.900	378	3.852	2.575	0.1508	1.837
002	3.510	3.509	25.370	471	4.038	2.609	0.1469	1.950
101	3.290	3.290	27.080	505	3.581	2.645	0.1429	2.081
102	2.554	2.555	35.090	265	3.394	2.877	0.1208	2.697
110	2.151	2.151	41.960	188	2.574	3.166	0.0997	3.225
103	1.980	1.980	45.770	236	3.731	3.375	0.0877	3.518
200	1.863	1.863	48.830	192	2.733	3.577	0.0781	3.753
112	1.834	1.834	49.670	201	3.059	3.638	0.0755	3.818
201	1.800	1.800	50.660	173	2.870	3.715	0.0724	3.894
202	1.645	1.645	55.820	159	3.272	4.191	0.0569	4.291
203	1.456	1.457	63.830	144	3.888	5.339	0.0350	4.906
210	1.407	1.406	66.440	154	2.641	5.891	0.0288	5.107
211	1.380	1.380	67.820	182	2.811	6.239	0.0256	5.213
105	1.312	1.311	71.960	121	5.264	7.603	0.0172	5.531
212	1.305	1.305	72.350	126	3.271	7.769	0.0165	5.561

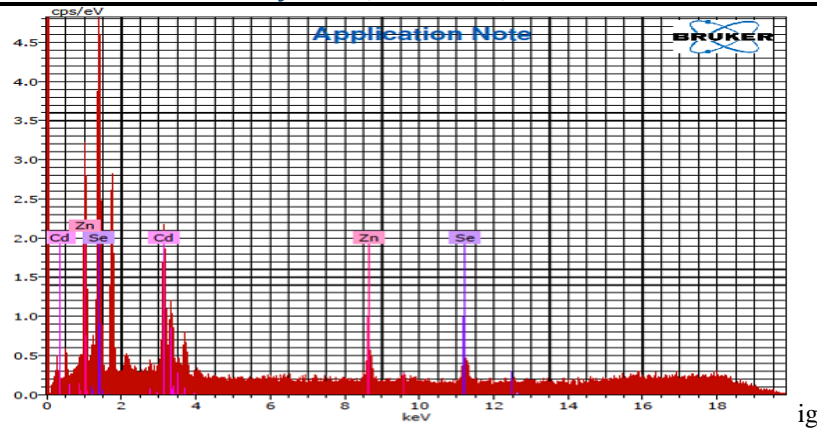
Table 2. X-ray diffractogram (XRD) JCPDS cubic data for $Zn_{0.75}Cd_{0.25}Se$ sample of thickness 1500 Å⁰

[hkl] values from JCPDS data	d(Å) values from JCPDS data of znse	Observed values of d(Å) $Zn_{0.75}Cd_{0.25}Se$	Observed $(2\theta)^{\circ}$ values of peaks	intensity	Lattice parameter a(Å)	Particle size D (Å)	Dislocation density δ ($\times 10^{15}$ lines/m ²)	Micro strain (ϵ_s)
111	3.273	3.273	27.230	492	3.703	2.648	0.1426	2.093
200	2.835	2.836	31.520	334	3.486	2.762	0.1310	2.423
220	2.004	2.005	45.200	208	3.466	3.342	0.0895	3.474
311	1.707	1.708	53.600	186	3.730	3.968	0.0635	4.120
222	1.635	1.635	56.150	139	3.830	4.228	0.0559	4.316
400	1.417	1.417	65.840	175	4.242	5.674	0.0310	5.061
331	1.300	1.300	72.650	119	4.548	7.896	0.0160	5.584
420	1.267	1.267	74.840	124	4.648	9.005	0.0123	4.753

Scanning Electron Microscope - SEM is a promising technique for the topography study of $Zn_{0.75}Cd_{0.25}Se$ thin film sample, coz it provides us information regarding the growth mechanism and shape and size of the particles in thin films [2,6,11]. The SEM pictures of $Zn_{0.75}Cd_{0.25}Se$ thin films of thickness 1500 Å deposited on glass substrates are shown in Figure 3. The morphological study of $Zn_{0.75}Cd_{0.25}Se$ thin film by SEM image reveals the well adhesive uniform surface nature on glass substrate. The SEM pictures also show that very small, fine and hardly distinguishable grains are smeared all over the surface [11,12]. The cracks on the surface of the $Zn_{0.75}Cd_{0.25}Se$ thin films were not observed. The spherical and flower-like shape of the particles can be easily observed SEM images [8]. SEM observations show the crystalline growth for the deposited $Zn_{0.75}Cd_{0.25}Se$ thin films [4,15]. The present work of SEM investigations is done at K.B.C.N.M.U., Jalgaon.

Fig 3: SEM pictures for $Zn_{0.75}Cd_{0.25}Se$ films (a)400 nm, x = 120k(b)500 Nm, x = 60k(c)1.0 μm, x = 30k(d)2.0 μm, x =20k

Energy-dispersive X-ray spectroscopy - The presence of elemental constituents in Zn doped CdSe ($Zn_{0.75}Cd_{0.25}Se$) thin film is confirmed from EDAX analysis [10]. The $Zn_{0.75}Cd_{0.25}Se$ films were deposited on glass substrates shows that the content of Cd and Zn is less than the percentage present in the starting material. However, the selenium content is always present in stoichiometric percentage which nearly equal to starting material [10]. These results show the n-type nature of these $Zn_{0.75}Cd_{0.25}Se$ thin films as Selenium is present in a more proportion [12-14].



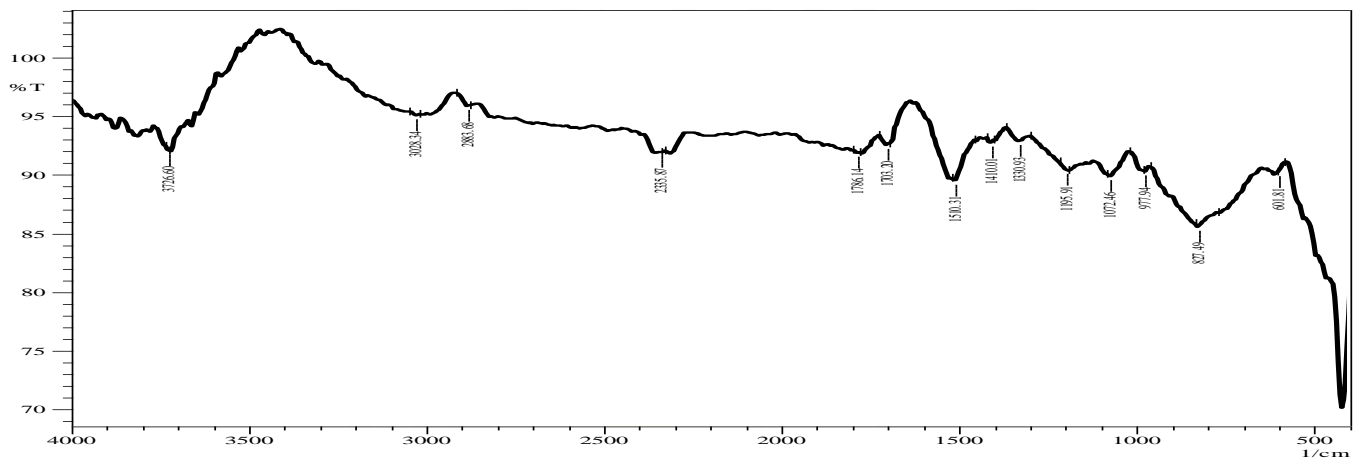
Element		Zn _{0.75} Cd _{0.25} Se	
		Mass %	Atomic %
Zn	30	11.69	15.65
Se	34	47.15	52.29
Cd	48	41.16	32.06

4:- EDAX spectra of Zn_{0.75}Cd_{0.25}Se

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

Fourier-Transform Infrared Spectroscopy - FT-IR technique can be used to detect the defects and the impurity contents in thin films. The present compound was made up three atoms such as Zinc, Cadmium and Selenium FT-IR may also be carried-out to understand the molecular structure of the Zn_{0.75}Cd_{0.25}Se thin film[1-4]. The FT-IR transmission spectrum of Zn_{0.75}Cd_{0.25}Se thin film in the range of our interest (500–4000 cm⁻¹) is displayed in Fig. 5. The FT-IR analysis shows that the characteristic vibration mode occurs at peak number 601cm⁻¹. [8,10] The other peaks are at 827 cm⁻¹, 1072 cm⁻¹, 1330 cm⁻¹, 2335 cm⁻¹, and 3028 cm⁻¹ are the finger print spectral peaks of Zn_{0.75}Cd_{0.25}Se film formation. This observation shows that the increased crystalline nature of the vacuum deposited Zn_{0.75}Cd_{0.25}Se thin films of thickness 1500 Å by increasing vacuum[11,12].

Fig 5 - FTIR result of Zn_{0.75}Cd_{0.25}Se thin films



Atomic Force Microscopy (AFM) - Figures given below illustrate 2-D and 3-D AFM images of Zn_{0.75}Cd_{0.25}Se thin films deposited on cleaned glass substrates[3,4]. All vacuum deposited films at thickness 1500 Å indicate better morphology. On the other hand, root mean square (RMS) roughness is defined as the standard deviation of the surface height profile from the average height, is the most commonly reported measurement of surface roughness [7]. The root mean square (Rq), the average roughness (Ra), average grain size and maximum height of the deposited Zn_{0.75}Cd_{0.25}Se thin films are shown in the table (4).

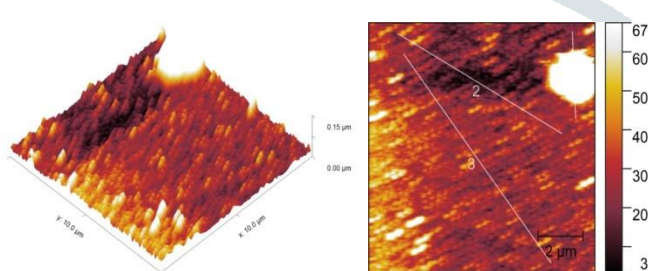


Fig 6 (a) sample 1 of Zn_{0.75}Cd_{0.25}Se

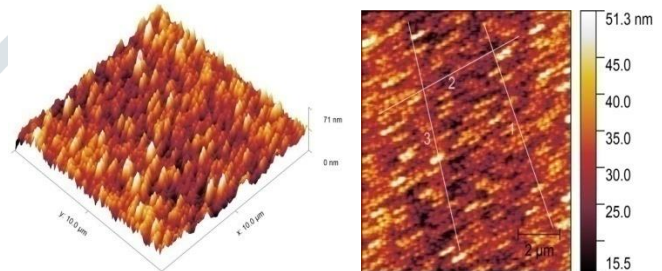


Fig 6 (b) sample 2 of Zn_{0.75}Cd_{0.25}Se

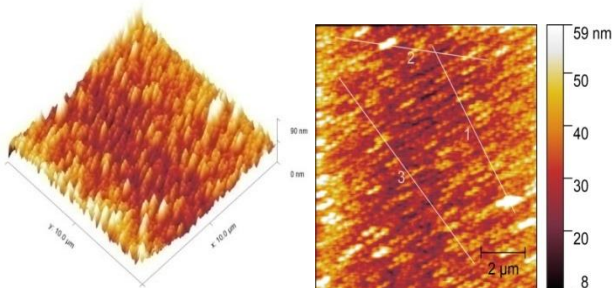


Fig 6 (c) sample 3 of Zn_{0.75}Cd_{0.25}Se

Sample of Zn _{0.75} Cd _{0.25} Se	Roughness average (nm)	Root mean square (nm)	Max. peak height (nm)	Average grain size (nm)
Sample 1	6.588	8.517	55.164	34.947
Sample 2	5.047	6.426	40.441	30.161
Sample 3	11.140	18.342	117.60	30.971

Table 4 AFM parameters of Zn_{0.75}Cd_{0.25}Se

IV. CONCLUSION

From **XRD** It is found that the deposited Zn doped CdSe films i.e. $Zn_{0.75}Cd_{0.25}Se$ of thickness 1500 Å show wurtzite structure along crystallographic planes (100), (002), (101),(102),(110) and (103) and for cubic structure the preferred crystal orientation is along (111), (200), (220),(311) and (400) planes. The XRD analysis shows that the films are polycrystalline in nature. The lattice parameters of $Zn_{0.75}Cd_{0.25}Se$ are almost matching with the JCPDS data of CdSe and ZnSe. The values of lattice constant (a) are 3.428 Å and 3.956 Å, the average particle size (D) 4.347 Å and 4.940 Å, Dislocation density (δ) 0.0769 and 0.0677 and Micro strain (ϵ_s) 3.825 and 3.973 for wurtzite and cubic structure respectively.

The **SEM** shows uniform growth of Zn doped CdSe i.e. $Zn_{0.75}Cd_{0.25}Se$ films on a glass substrate. The particles of $Zn_{0.75}Cd_{0.25}Se$ thin films are spherical and flower-like in shape. The results of SEM show that the sizes of grain were 154 nm to 234 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 $Zn_{0.75}Cd_{0.25}Se$ thin film.

The **FT-IR** analysis of $Zn_{0.75}Cd_{0.25}Se$ thin films shows that the vibration mode occurs at peak number 601cm^{-1} , 827cm^{-1} , 1072cm^{-1} , 1330cm^{-1} , 2335cm^{-1} , and 3028cm^{-1} . The crystalline nature of $Zn_{0.75}Cd_{0.25}Se$ thin films increases by increasing vacuum.

AFM studies shows that, Average Roughness increases from 5.047 nm to 11.140 nm, the root mean square surface of the films is increase from 6.426 to 18.342 nm and the average grain size is increased from 30.161 to 34.947 nm in different samples of $Zn_{0.75}Cd_{0.25}Se$ thin film.

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