Comparative Study of Characterization of CdSe, ZnSe and $Cd_{0.5}Zn_{0.5}Se$ Thin Films Prepared by Vacuum Deposition Technique

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Abstract: The Cadmium Selenide (CdSe) and The Zinc Selenide (ZnSe) are binary compounds of II-VI group were zinc doped cadmium selenide ($Cd_{0.5}Zn_{0.5}Se$) is a ternary compound of II-VI group. All of these are very important semiconducting alloys for electronics and optoelectrical applications. The Thin films of CdSe, ZnSe, and $Cd_{0.5}Zn_{0.5}Se$ were deposited on a cleaned glass substrate by vacuum deposition technique under the pressure of ~10^{-5} mbar. In this research paper, we have studied thin films of a thickness of 1000 Å of CdSe, ZnSe, and $Cd_{0.5}Zn_{0.5}Se$. The ingot was formed by melt quench method of granules of core cadmium, granules of core zinc and powder of core selenium of Sigma Eldritch having purity 99.99. A powder of CdSe, ZnSe, and $Cd_{0.5}Zn_{0.5}Se$ obtain by grinding ingot in a porcelain pot. The powder obtained from ingot is then heated in molybdenum boat up to 700 ^{0}C to 1100 ^{0}C and current 110 A. In this present work we have studied the effect of Zinc content on morphological, compositional and structural properties in $Cd_{0.5}Zn_{0.5}Se$ thin films and compared the characteristics like XRD and SEM with that of CdSe and ZnSe thin films. The lattice parameter a, The particle size D and the hkl indices were also studied. The XRD pattern gives structural information of CdSe, ZnSe, and the $Cd_{0.5}Zn_{0.5}Se$ thin films. Scanning electron microscopy (SEM) gives us the surface morphological images of CdSe, ZnSe, and $Cd_{0.5}Zn_{0.5}Se$ thin films.

***Index Terms* -** Thin film, CdSe, ZnSe, $Cd_{0.5}Zn_{0.5}Se$, Crystal Structure, XRD, Surface Morphology, SEM, vacuum

I. INTRODUCTION

As we know that the semiconductor industry is increasing rapidly worldwide due to the use of semiconductors in each and every sector of electronics [1]. In this paper, we have studied comparative data of characterizations of cadmium selenide (CdSe) and zinc selenide (ZnSe) and zinc doped cadmium selenide ($Cd_{0.5}Zn_{0.5}Se$) thin films of thickness 1000 Å. Both cadmium selenide (CdSe) and zinc selenide (ZnSe) are binary were zinc doped cadmium selenide ($Cd_{0.5}Zn_{0.5}Se$) is a ternary compound from II–VI group [2]. All these compounds can be found in hexagonal as well as cubic crystal structures and crystalline in nature. Due to wide bandgap ranges, II-VI group compounds semiconductor has a lot of applications in optoelectronics devices like thin film transistors, photo-detectors, gas sensors, light amplifiers, lasers, light emitting diodes, large-screen liquid crystal display, etc. [3, 4]. The use of crystalline cadmium selenide (CdSe), zinc selenide (ZnSe) and zinc doped cadmium selenide ($Cd_{0.5}Zn_{0.5}Se$) thin films have attracted much interest in an expanding variety of applications in various electronic and optical fields.[5, 6]. A number of thin film deposition methods, such as electron beam pumping, thermal evaporation, molecular beam epitaxy, chemical bath deposition (CBD), vacuum deposition technique, etc. have been used for preparing cadmium selenide (CdSe) , zinc selenide (ZnSe) and zinc doped cadmium selenide ($Cd_{0.5}Zn_{0.5}Se$) thin films thin films [7– 9]. We have prepared cadmium selenide (CdSe), zinc selenide (ZnSe) and zinc doped cadmium selenide ($Cd_{0.5}Zn_{0.5}Se$) thin films by the vacuum deposition technique [10–12]. A Number of researchers studied CdSe, ZnSe but the effect of zinc content and thickness on physical properties of $Cd_{0.5}Zn_{0.5}Se$ thin films is rarely presented in the literature. [1,2,7].

Today semiconductor industry relies on vacuum deposited thin film technology [3,18]. To deposit the thin films of CdSe, ZnSe and $Cd_{0.5}Zn_{0.5}Se$ we have used vacuum deposition technique which is one of the fast synthesis methods to produce high-quality thin films on a large scale [19]. This technique has many advantages compared to the other sophisticated techniques, like simple mechanism, high deposition rate, reproducibility, and economically viability [20]. CdSe, ZnSe and $Cd_{0.5}Zn_{0.5}Se$ thin films of a thickness of 1000 Å were deposited on a cleaned glass substrate by vacuum deposition technique under a vacuum of 10^{-6} Torr in Hind Hivac 12A4-D vacuum coater machine [14]. Preparative parameters such as high vacuum pumps like the rotary pump and diffusion pump, gauges are optimized to get good quality adherent and uniformly deposited thin films of CdSe, ZnSe and $Cd_{0.5}Zn_{0.5}Se$ [12]. The Crystal structure and lattice parameters of CdSe, ZnSe and $Cd_{0.5}Zn_{0.5}Se$ thin film of thickness 1000 Å were obtained by XRD and surface morphology of film studied by SEM characteristics [1 - 4].

II. EXPERIMENTAL

(A)Thin Film Deposition

The glass slides were used for thin film deposition in a vacuum unit. Slides first washed in a detergent soap solution then in distilled water followed by acetone to remove the impurities from glass surfaces. [1,2]. Thin films CdSe, ZnSe, and $Cd_{0.5}Zn_{0.5}Se$ were deposited by vacuum deposition technique at the vacuum of ~10^{-5} Torr. The vacuum deposition unit has a rotary pump, diffusion pump, Pirani Gauge for measuring low vacuum up to 10^{-3} Torr and Penning Gauge which measures a relatively high vacuum from 10^{-2} to 10^{-5} Torr [3,4]. Ingots of source material of cdse were obtained by mixing pure granules of Cd and Se, ingots of znse are obtained by mixing pure granules of Zn and Se and, a compound of Zn doped CdSe [$Cd_{0.5}Zn_{0.5}Se$] 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 we have used are of Sigma Aldrich company having a purity of 99.99 %[5-9]. The uniformly mixed compound of CdSe, ZnSe, and $Cd_{0.5}Zn_{0.5}Se$ were 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 in a vacuum unit. The deposition rate was maintained (02 - 06 Å/sec) throughout the preparation of thin films [13-14]. The source temperature varies from 700 ^{0}C to 1100 ^{0}C and current 110 A at which source material of different compounds start evaporation. The 230V low tension (LT) supply for evaporation source is obtained from a transformer by means of parallel connections in the secondary side of the transformer [19,20]. The substrates temperature kept constant by a continuous flow of cold water from a tap. The films of CdSe, ZnSe, and $Cd_{0.5}Zn_{0.5}Se$ of thicknesses 1000 Å were deposited under the almost same environment. The thickness monitor provided by Hind-High Vac using which the different thickness of thin films was monitored [21]. The different preparation parameters have been varied and optimized for uniform deposition of thin films of CdSe, ZnSe, and $Cd_{0.5}Zn_{0.5}Se$. To avoid oxidation of the films deposited, the system was allowed to cool down to room temperature for 20 minutes after completing the deposition process, without disturbing all the vacuum conditions [12]. The vacuum chamber has been cleaned after every deposition and the grease has been applied to rubber gasket before each run to attain the desired vacuum in the chamber. The uniform, porous free and well adhered thin films of CdSe, ZnSe, and $Cd_{0.5}Zn_{0.5}Se$ of thickness 1000 Å with the glass plates have been obtained [13-15].

B) *Characteristics*

The X-ray diffraction (XRD) was used to investigate the structure of cadmium selenide (CdSe), zinc selenide (ZnSe) and zinc doped cadmium selenide ($Cd_{0.5}Zn_{0.5}Se$) thin films of thickness 1000 Å. The particle size (D) is calculated using the Scherer's formula from the full width at half maximum β (FWHM) [3].

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

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

By applying Bragg's law the interplanar spacing '*d*' in the crystal has been determined using the X-rays of known wavelength and to measure the angle of diffraction 2θ of the most intense peak[18]. The structure of the films was evaluated by X-ray diffractometer using nickel-filtered copper Kα of wavelength λ=1.54060 Å, the formula is given as, [10 - 14].

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

where'd' is lattice spacing, 'λ' is a wavelength of monochromatic X-rays, 'θ' is the angle between the incident beam and the planes (hkl), '*n*' is the order of reflection (n = 1, 2, 3,4…..)

The lattice parameter (a) of thin films for the hexagonal and cubic structure is determined by using the following expression [17].

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

SEM is the most suitable technique for the topography and Surface morphological study of the CdSe, ZnSe, and $Cd_{0.5}Zn_{0.5}Se$ thin film. SEM gives valuable information regarding the shape, size and growth mechanism of the particles and/or grains in the CdSe, ZnSe, and $Cd_{0.5}Zn_{0.5}Se$ thin films [21]. The results of the XRD and the SEM of CdSe, ZnSe, and $Cd_{0.5}Zn_{0.5}Se$ thin films were studied in the next section and compared their results.

III. RESULTS AND DISCUSSIONS

For the structural analysis of the ZnSe, CdSe and $Cd_{0.5}Zn_{0.5}Se$ thin films, X-ray diffraction (XRD) technique is used [1,5]. 'd' value calculated using Bragg's equation. The hkl indices are obtained by comparing the x-ray diffraction data of deposited ZnSe, CdSe and $Cd_{0.5}Zn_{0.5}Se$ thin films with the Joint Committee on Powder Diffraction Standard (JCPDS) data cards [7,10]. This data of x-ray diffraction can also be used to determine the structural factors, particle size, etc [11]. The structural properties of the ZnSe, CdSe and $Cd_{0.5}Zn_{0.5}Se$ thin film of 1000 Å thickness were studied by the X-ray diffractometer (XRD) using Cu Kα radiation (l = 1.54060 Å) [20]. Scan angle with angular range 05° ≤ 2θ ≤ 80° at 40 kV voltages and 40 mA current is used in XRD. 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 the 0.406 [18]. 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 zinc dopes cadmium selenide i.e. $Cd_{0.5}Zn_{0.5}Se$ [19]. The bands in the CdSe spectrum are typical for hexagonal structure of CdSe of crystallographic planes (100) at 23.900^o, (101) at 27.080^o, (102) at 35.090^o, (110) at 41.960^0 , and (103) at 45.770^o (JCPDS 08-0459) [10, 14]. On the other hand, the bands in the ZnSe spectrum are typical for the cubic structure of crystallographic planes (111) at 27.230^o, (220) at 45.200^o, (311) at 53.600^o, and (400) at 65.840^o respectively (JCPDS 19 - 0191) [20-21]. The Zn doped CdSe i.e. $Cd_{0.5}Zn_{0.5}Se$ 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 [1-3].
The XRD patterns of crystalline CdSe, ZnSe and Zn doped CdSe [$Cd_{0.5}Zn_{0.5}Se$] thin film is shown in Figure 1, 2 and 3

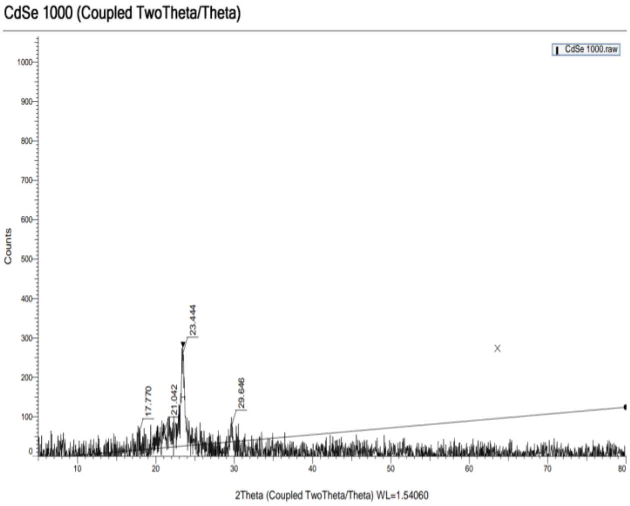

Fig. 1: XRD of **CdSe** films of thickness 1000 Å

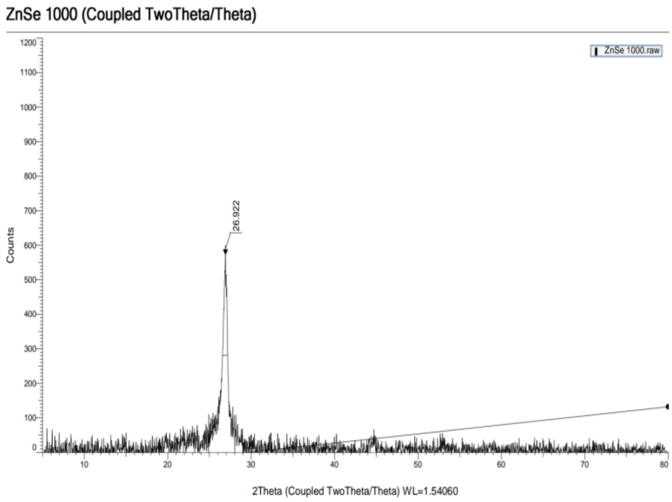

Fig. 2: XRD of **ZnSe** films of thickness 1000 Å

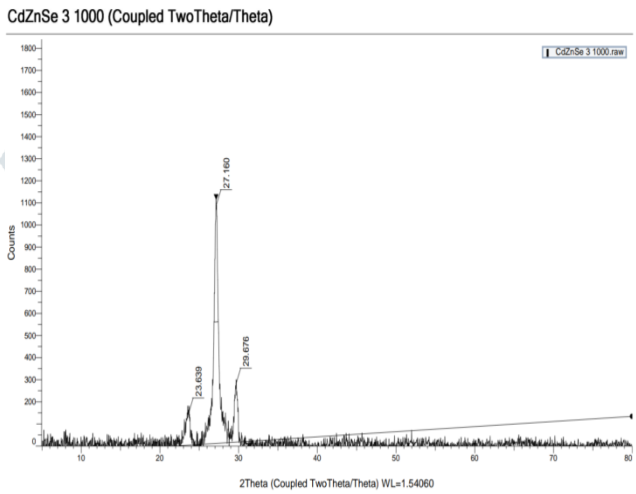

Fig. 3: XRD of $\mathbf{Cd_{0.5}Zn_{0.5}Se}$ films of thickness 1000 Å

Table 1. X-ray diffractogram (XRD) JCPDS hexagonal data for $\mathbf{Cd_{0.5}Zn_{0.5}Se}$ and **CdSe** sample of thickness 1000 A^0

[hkl] values from JCPDS data	d(Å) values from JCPDS data of cdse	Observed values of d(Å) **CdSe**	Observed (2ɵ)° values of peaks	intensity	Observed values of d(Å) $\mathbf{Cd_{0.5}Zn_{0.5}Se}$	Observed (2ɵ)° values of peaks	intensity	Lattice parameter a(Å)	Particle size D (Å)
100	3.720	3.720	23.900	586	3.720	23.900	597	3.724	3.645
002	3.510	3.509	25.370	514	3.509	25.370	573	4.972	3.655
101	3.290	3.290	27.080	516	3.290	27.080	1565	4.652	3.668
102	2.554	2.555	35.090	324	2.555	35.090	320	5.713	3.740
110	2.151	2.151	41.960	215	2.151	41.960	274	3.041	3.820
103	1.980	1.980	45.770	229	1.980	45.770	240	6.261	3.871
200	1.863	1.863	48.830	189	1.863	48.830	219	3.722	3.917
112	1.834	1.834	49.670	201	1.834	49.670	195	4.492	3.930
201	1.800	1.800	50.660	192	1.800	50.660	202	4.024	3.946
202	1.645	1.645	55.820	193	1.645	55.820	184	4.652	4.036
203	1.456	1.457	63.830	195	1.457	63.830	175	5.249	4.202
210	1.407	1.406	66.440	173	1.406	66.440	163	3.146	4.263
211	1.380	1.380	67.820	161	1.380	67.820	163	3.338	4.297
105	1.312	1.311	71.960	155	1.311	71.960	162	6.668	4.407
212	1.305	1.305	72.350	158	1.305	72.350	149	3.915	4.418
300	1.241	1.239	76.820	140	1.239	76.820	156	3.723	4.552
301	1.221	1.221	78.170	118	1.221	78.170	142	3.861	4.595

Table 2. X-ray diffractogram (XRD) JCPDS cubic data for **$Cd_{0.5}Zn_{0.5}Se$** and **ZnSe** sample of thickness 1000 A^0

[hkl] values from JCPDS data	d(Å) values from JCPDS data of znse	Observed values of d(Å) **ZnSe**	Observed (2ɵ)° values of peaks	intensity	Observed values of d(Å) **$Cd_{0.5}Zn_{0.5}Se$**	Observed (2ɵ)° values of peaks	intensity	Lattice parameter a(Å)	Particle size D (Å)
111	3.273	3.273	27.230	721	3.273	27.230	1591	5.669	3.670
200	2.835	2.836	31.520	418	2.836	31.520	447	5.670	3.706
220	2.004	2.005	45.200	279	2.005	45.200	258	5.670	3.863
311	1.707	1.708	53.600	223	1.708	53.600	208	5.661	3.996
222	1.635	1.635	56.150	199	1.635	56.150	205	5.663	4.042
400	1.417	1.417	65.840	160	1.417	65.840	215	5.668	4.249
331	1.300	1.300	72.650	144	1.300	72.650	143	5.666	4.427

The surface morphological study by SEM images of CdSe thin films of thickness 1000 Å on glass substrates is shown in Figure 4. The rectangular and rod-like shape of the particles can be observed easily in high magnification micrographs [5, 11]. The SEM observations of a deposited CdSe thin films show the crystalline growth of thin film on a glass substrate [13].
The SEM images of ZnSe thin films of thickness 1000 Å on glass substrate are shown in Figure 5. The oval-like shape of the particles, well adhesive uniform surface nature of the particles can be observed easily under high magnification micrographs [17]. The SEM images show the crystalline growth for the deposited ZnSe thin films [18].
The SEM is a promising technique, as it gives us information regarding the growth mechanism, shape, and size of the particles in thin films [10-11]. The SEM pictures of $Cd_{0.5}Zn_{0.5}Se$ thin films of thickness 1000 Å deposited on a glass substrates are shown in Figure 6. The Surface morphological study by SEM image of the deposited film shows the well adhesive uniform crystalline surface nature of films on a glass substrate [14-16]. The spherical and flower-like shape of the particles can be observed easily in SEM images and No crack was observed on the surface of the $Cd_{0.5}Zn_{0.5}Se$ thin films [21].

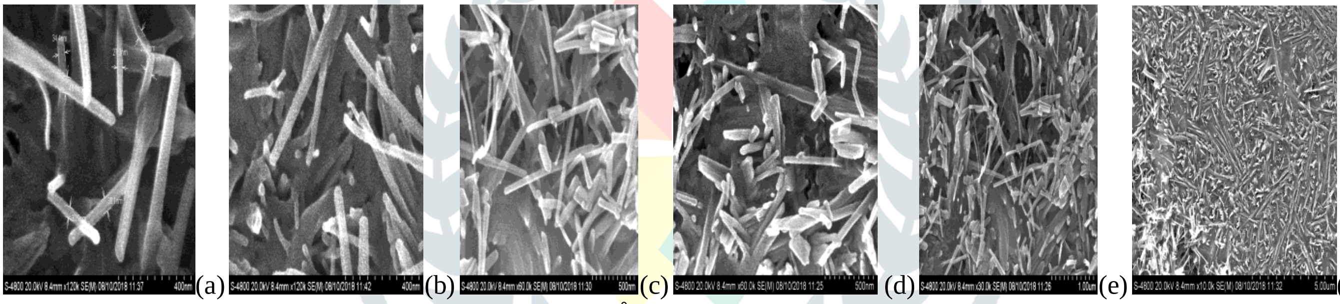

Fig 4: SEM images of CdSe thin film of thickness 1000 Å (a) 400nm (b) 400nm (c) 500nm (d) 500nm (e) 1μm (f) 10μm

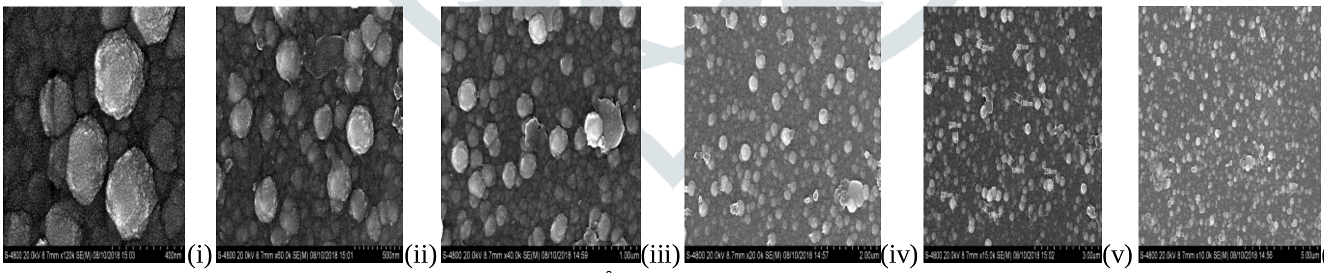

Fig 5: SEM images of ZnSe thin film of thickness 1000 Å (i) 400nm (ii) 500nm (iii) 1μm (iv) 2μm (v) 3μm (vi) 5μm

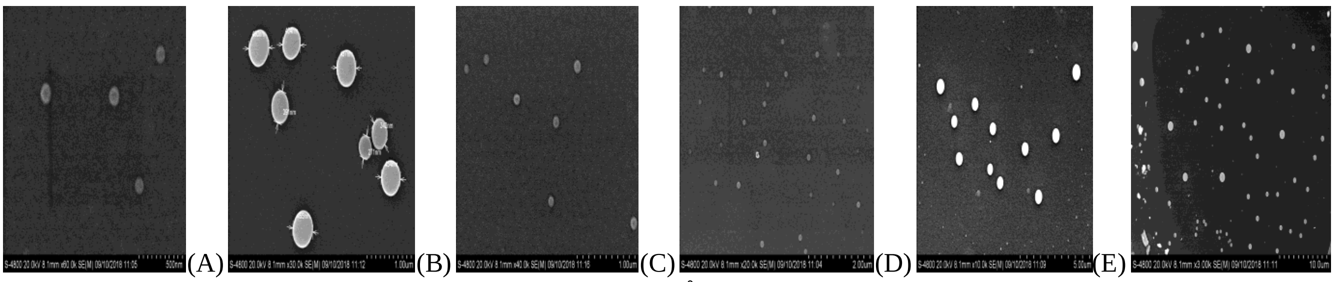

Fig 6: SEM images of $Cd_{0.5}Zn_{0.5}Se$ thin film of thickness 1000 Å (A) 500nm (B) 1μm (C) 1μm (D) 2μm (E) 5μm (F) 10μm

IV. CONCLUSION

From XRD It is found that The CdSe thin films having hexagonal structure along crystallographic planes (100),(101),(102),(110) and (103) and crystalline in nature. The XRD of the ZnSe thin films shows cubic structure along crystallographic planes (111), (220),(311) and (400) and are crystalline in nature. while XRD pattern of Zn doped CdSe films $Cd_{0.5}Zn_{0.5}Se$ shows hexagonal structure along crystallographic planes (100),(101),(102),(110) and (103) and cubic structure with preferred crystal orientations along (111), (220),(311) and (400) planes and the polycrystalline in nature of $Cd_{0.5}Zn_{0.5}Se$ thin films. The lattice parameters are almost matching with the JCPDS (08-0459) data of CdSe and JCPDS (19 - 0191) data of ZnSe. The value of lattice constant 'a' is 4.425 Å and the average particle size D is 4.088 Å for hexagonal structure. The value of lattice constant 'a' is 5.666 Å and the average particle size D is 4.055 Å for cubic structure.
The SEM result of the surface of CdSe, ZnSe, and $Cd_{0.5}Zn_{0.5}Se$ thin films shows the uniform growth of films on a glass substrate. The particles of cdse are rod shape and rectangular in shape having size 26 nm o 38 nm. The particles of znse are spherical and flower-like in shape having size 180nm to 270 nm. The result of SEM for $Cd_{0.5}$ $Zn_{0.5}Se$ shows that the grains are spherical in shape and sizes of grain are from 134 nm to 460 nm. SEM shows uniform growth of ZnSe on a glass substrate. The particles are spherical in shape with size in the submicron range.

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