Synthesis and characterization of nanocrystalline Zinc Selenide thin films prepared by chemical bath deposition method

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ABSTRACT

Zinc selenide (ZnSe) thin films have been deposited using chemical bath deposition method (CBD) on glass substrate at 70ºC. The deposition parameter of ZnSe thin film is interpreted in the present investigation. The as-deposited films were annealed in air for 1h. The prepared films were characterization by X- ray diffraction (XRD), UV-vis spectroscopy and dc-electrical measurements. XRD study revealed that the ZnSe thin films are polycrystalline in nature and have a cubic (zinc blend) structure. The structural parameters such as particle size (D), strain (ε) and dislocation density (δ) values in the films were calculated. The average grain size is in the range of (10-30 nm). The values of optical direct energy gap E_g have been determined from the absorption spectra. The energy gaps of the films were found to lie in the range between (2.72- 2.82 eV). Temperature resistivity measured in the range (300-560 K) showed a change in conduction mechanism at (350 K). The room temperature electrical resistivity is in the order of $10^6 \Omega$.cm. Thus prepared ZnSe thin films can be used as a window layer in solar cells due its wide direct band gap and high electrical resistivity properties.   © 2014 Trade Science Inc. - INDIA

KEYWORDS

1 INTRODUCTION

Semiconductor nanocrystals are of ever-increasing research interest, due to the unique optical properties demonstrated by those quantum-confined nanoparticles such as quantum dots (0 diminutions), wires (1diminution) and sheets (2diminution)[1]. Among various semiconductor nanoparticles, Zinc selenide (ZnSe), most important (II-VI) group of semiconductors, have attracted considerable attention because of their novel physical properties such as, wide-band gap (2.7), higher luminescent efficiency, low absorption coefficient and excel-lent transparency to infrared range, so it has considered as a prospective material for the fabrication of optoelectronic devices, such as blue–green laser diodes[2]. Besides, ZnSe also has potential application in optically controlled switching due to its giant photo resistivity[3]. ZnSe synthesized by several methods such as, microwave-irradiation[4], sol gel[5], hydrothermal[6], vacuum deposition technique[7], successive ionic layer adsorption and reaction (SILAR)[8], electrodeposited[9] and chemical bath deposition[10]. Among these methods (CBD) has greater advantages than others for several reasons, (CBD) is quiet simple, low cost, simplicity, it is

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one of the more versatile techniques for thin films growth, it is quite appropriated for large area deposition, which can be very convenient for large scale solar cell fabrication and it is produces homogeneous and high-quality thin films[11]. The properties of thin films deposited by (CBD) technique can be controlled by several parameters such as PH of the solution, temperature and time deposition. In the present work we describe the deposition of ZnSe films onto the glass substrate from aqueous alkaline medium using selenourea as a selenide ion source. The preparation parameters such as concentration of Zn^{2+} and Se^{2-} ion source, deposition time and PH have been optimized in order to obtain good quality ZnSe films. The ZnSe films characterization including structural, optical and electrical properties. In order to study the influence of annealing on the film properties, the ZnSe films were annealed at 100, 200, 300 and 400 R"C in air atmosphere for 1h.

EXPERIMENTAL

The ZnSe thin films were deposition on commercial glass slides (2.5x7.5x2 cm³) by the (CBD) technique using the procedure described previously[12] at temperature of 70°C and with deposition time of 30 minute. The glass slides were cleaned with soap and, dried, degreased with ethanol in ultrasonic cleaner and kept immersed in distilled water prior to the deposition. The cleaned glass substrates were clamped vertically with plastic clamps and kept immersed in a stirred solution for 30 minute. The deposition of ZnSe on glass substrate is based on slow release of Zn^{+2} and Se^{-2} ions in a solution which then condenses onto the substrate. For this Zn salt zinc acetate [$(CH_3COO)_2Zn$] with a suitable complexing agent (ammoniaNH_3) is used as a Zn^{+2} source and selenosulphate (Na_2SeSO_3) as a Se^{+2} source in alkaline medium (pH=11). Chemicals used for the deposition of ZnSe thin films were Zinc acetate, sodium sulphate (Na_2So_3), selenium metal, ammonia solution (25%), sodium Hydroxide (NaOH) and hydrazine hydrate (N_2H_2, $2H_2O$). All chemicals used were A.R. Grade, supplied by Oxford Laboratory of Mumbai (India). The 0.25 mol/L sodium selenosulphate (Na_2SeSO_3) solutions were prepared by refluxing selenium powder (2.5g) with sodium sulphate (7.5g) in (100 ml) distilled water for 8 hours at 70 °C. The mixture remained under constant stir-

ring throughout reflux process. Selenosulphate is produced according to following equation:

$$Na_2SO_3 + Se \rightarrow Na_2SeSO_3 \qquad (1)$$
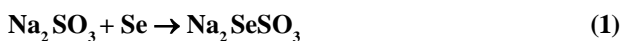
Three different starting chemical baths were prepared S1, S2 and S3 with different concentration of zinc acetate. Where S1 (0.25 mol/L Zinc acetate, 0.25 mol/L sodium selenosulphate), S2 (0.3 mol/L Zinc acetate, 0.25 mol/L sodium selenosulphate and S3 (0.4 mol/L Zinc acetate, 0.25 mol/L sodium selenosulphate). To prepare sample S1, solution a 25 ml of 0.25M zinc acetate solution was taken in a beaker of 200 ml capacity then adding 1 ml of hydrazine hydrate (80%) under a constant stirring. To this solution, under constant stirring, a sufficient amount of ammonia solution (25%) was added to dissolve the turbidity of the solution. The pH 11 of their sultan solution was adjusted by adding sodium hydroxide (1 M) solution. Then the reactant vessel was kept in a constant temperature water bath. When appropriate temperature of 70 °C was reached, sodium selenosulphate (0.25 M, 25 ml) solution was added to the bath and glasses substrates were kept vertically in the bath. After the deposition the samples were removed from the bath and washed in distilled water until heterogeneities are removed. Then they were dried in air. Optical properties of chemical bath deposited ZnSe thin films were measured at room temperature by using UV-VIS spectrophotometer Cary 50 Cm-Exlena in the wavelength range of (300-800 nm). The film thickness was determined gravimetrically by measuring the change in weight of the substrate due to film deposition, the area of deposition and using the known density of ZnSe. The values of films thickness are 0.608, 0.62 and 0.635 µm for S1, S2 and S3 respectively. X-ray diffraction study of ZnSe thin films were carried out with CuKα radiation (λ= 1.5405Å) using Philips pw 1710 diffract meter in the range of the diffraction angle 5° - 80°. The electrical resistivity of the films was measured by the van der paw techniques. For this purpose silver paint electrodes of (2 mm) length at (2 mm) separation were painted of the samples in a coplanar configuration. All films were annealed in air for 1h.

RESULTS AND DISCUSSION

Reaction mechanism

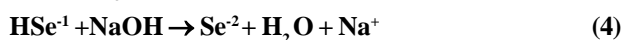The decomposition of sodium selenosulphate is

made possible in an aqueous alkaline medium Containing ammonia as a complexing agent that allows controlling the Zn^{2+} and to have a soluble pecies of Zn^{2+} in the reaction bath

The chemical equations of ZnSe thin films deposition described as follows;

When ammonia solution is added in Zn-salt solution to form the complex zinc tetra-amine ion $[Zn(NH_3)_4^{2+}]$ as,

$$(CH_3COO)_2 Zn + 4NH_3 \rightarrow [Zn(NH_3)_4]^{+2} + 2CH_3COO^- \quad (2)$$

Sodium selenosulphate hydrolyses in the solution to give Se^{2-} ions according to

$$Na_2SeSO_3 + NaOH \rightarrow Na_2SO_4 + HSe^{-1} + Na^+ \quad (3)$$

$$HSe^{-1} + NaOH \rightarrow Se^{-2} + H_2O + Na^+ \quad (4)$$

$$2CH_3COO^- + 2Na^+ \leftrightarrow 2CH_3COONa \quad (5)$$

Then $Zn(NH_3)_4^{+2}$ react with Se^- ions that results formation of ZnSe films as follows

$$[(Zn(NH_3)_4)]^{+2} + Se^{-2} \rightarrow ZnSe \downarrow + 4NH_3 \uparrow \quad (6)$$

The resultant films were homogenous, well adherent to glass substrate.

X-ray diffraction

Figure 1 Shows XRD patterns obtained for as-grown films deposited at different concentration of zinc acetate. The presence of well-defined peaks reveals the polycrystalline nature of the films. This XRD patterns exhibits prominent peaks at 2θ values of 27.4, 45.3 and 53.64 which could be indexed to scattering from the (111), (220) and (311) cubic phase ZnSe planes, respectively according to JCPDS file no.5555. And indicate a preferential orientation along the (111) direction. The (111) is the close packing direction of Zinc blende structure. Several studies have reported that ZnSe thin films are characterized as a Zinc-blende type structure with a preferred orientation along (111)[13-15]. The XRD patterns of ZnSe films showed broad peaks indicating the Nano-dimensions of the samples. The lattice spacing (d) can be calculate from the Bragg's formula

$$d = \frac{\lambda}{2sin\theta} \quad (7)$$

Where λ is the wavelength of X-ray used

The lattice parameter (a) has been calculated by the following expression:

$$a = d(h^2 + k^2 + l^2)^{1/2} \quad (8)$$

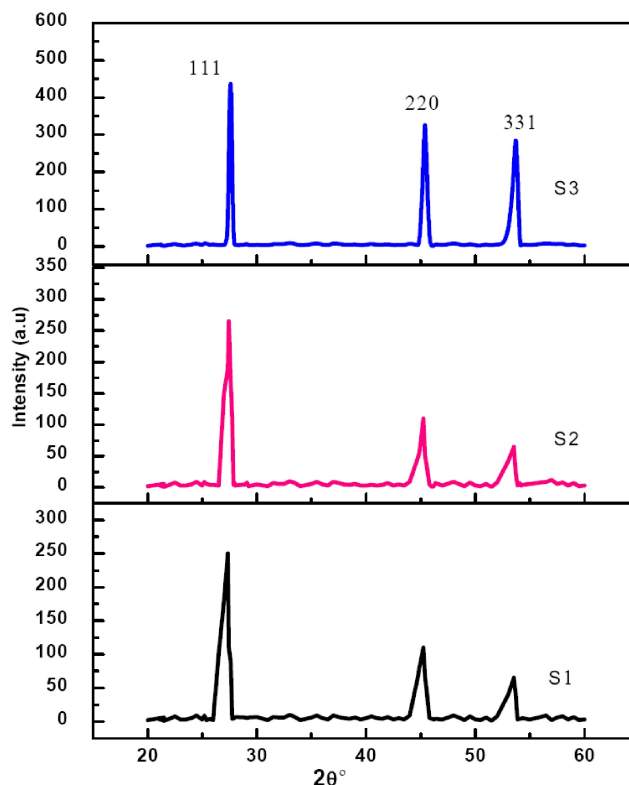Where h, k, l are the Miller indices of the lattice planes.

Figure 1 : XRD patterns of ZnSe thin films at different concentration of zinc acetate

The estimated lattice parameter of ZnSe thin films is in good agreement with the JEPDS data as shown in TABLE 1.

The particle size (D) is calculated using the Scherrer's formula from the full width at half maximum (β) (FWHM).

$$D = \frac{0.94\lambda}{\beta cos\theta} \quad (9)$$

Where D is the mean dimension of the crystallites, λ the wave length of X- ray and θ is the Bragg's angle. We use the standard (111) reflection at $2\theta = 27.3°$ to calculate D.

The dislocation density (δ) has been calculated by using the formula[16]

$$\delta = \frac{15\varepsilon}{aD} \quad (10)$$

The strain (ε) in the films was calculated use the relation[16]

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TABLE 1 : The calculated values of lattice constant (*a*), inter planar distance (*d*), crystallite size (*D*), dislocation density (δ) and strain (ε) for ZnSe thin films

ε X10^{-3}	δ X10^{14} lines/m^2	D (nm)	β (deg.)	a (Å)	d (Å) Observe	d (Å) JCPS	hkl	2 θ° Observe	2θ° JCPS	Samp.
6.2	1.64	10	1.487	5.643	3.258	3.265	111	27.35	27.3	S1
				5.6475	1.9967	1.985	220	45.38	45.4	
				5.6588	1.7062	1.708	311	53.67	53.7	
5.1	1.1	12.32	1.21	5.6229	3.2464	3.265	111	27.45	27.3	S2
				5.65	1.9976	1.985	220	45.36	45.4	
				5.6628	1.7074	1.708	311	53.63	53.7	
0.5	0.04	32.62	0.45	5.5929	3.2291	3.265	111	27.6	27.3	S3
				5.6393	1.9938	1.985	220	45.45	45.4	
				5.6393	1.7039	1.708	311	53.75	53.7	

$$\varepsilon = \frac{\beta \cos\theta}{4} \tag{11}$$

The structural parameters values for the films are given in TABLE 1.

Optical properties

The optical absorption spectra of ZnSe thin films were studies at room temperature in the wavelength of 350 - 1000 nm. Figure 3 shows the UV-visible absorption spectra of ZnSe thin films synthesized with different concentration of zinc acetate. From this figure it is clear that absorption edge shifted to the lower wavelength side with increase of concentration of zinc acetate. The absorption coefficient (α) of the films was calculated from the following equation:

$$\alpha = \frac{2.303 \, A}{t} \tag{12}$$

Where A is the absorbance and t is the thickness of the films. The optical band gap E_g has been calculated using Taucs formula[17]

$$(\alpha h\nu) = B(h\nu - Eg)n \tag{13}$$

Where hυ is incident photon energy, A is a constant, and the exponent n depends on type of transition, As

ZnSe is a direct band gap material, n =1/2 for the allowed transition. A plot of (αhυ)² versus hυ is shown in the Figure 5 the linear nature of the plot shows that the existence of direct transitions. Extrapolation of the linear portion of the curve to α² = 0 gives the band gap, which is about 2.86, 2.815 and 2.76 eV for samples S1, S2 and S3 respectively. The optical parameters values for the films are given in TABLE 2. The observed values of energy gaps are greater than standards band gap (2.7 eV) of the ZnSe bulk materials, showing a blue shift 0.15, 0.12 and 0.06 eV for samples S1, S2 and S3 respectively. This is attributed due to size quantization occurs due to localization of electrons and holes in confined volume of the semiconductor materials. It is well know that the band gap energy depends on the particle size, crystals structure and strain in the film. This blue shift in the absorption edge is consequence of the enhancement of the band gap of the

Semiconducting Nano crystals with the reduction of their sizes. The average particle size of the nanoparticles can be determined by using Brus equation[18]:

$$\Delta E = \left(\frac{\pi \hbar}{2R^2}\right)\left(\frac{1}{me} + \frac{1}{mh}\right) - \left(\frac{1.8e^2}{\varepsilon_1 R}\right) \tag{14}$$

TABLE 2 : Results of optical characteristics of the CBD ZnSe films

Particle size From XRD (nm)	Particle size from Brus eq. (nm)	Shift in band gap (eV)	Band gap From UV-vis	(deg)β	2θ°	Samples
10	7	0.16	2.86	1.487	27.35	S1
12.32	8	0.13	2.83	1.21	27.45	S2
32.6		0.06	2.76	0.468	27.6	S3

Where ΔE is the increase of the band gap energy, $\varepsilon 1$ is the dielectric constant, $\hbar$ ⚇ ⬍⬆♫π where h is plank constant and $m_e = 0.7$ m and $m_h = 1.7$ m are the effect mass of electron and holes respectively.

Applying Eq. (14), values 3.5 nm (the diameter is 7 nm) and 4. nm (the diameter 8 nm) has been estimated for the radius of the two nanoparticles ZnSe samples (S1) and (S2) respectively.

These values are slightly different with the sizes determined from XRD.

Effect of annealing in air on structure properties

Figure 6 shows the XRD patterns of the sample S2 annealed in air at 200, 300, 400 °C for 1h. XRD patterns of annealed films are very similar to the as-grown ones, indicating that a good morphology was obtained
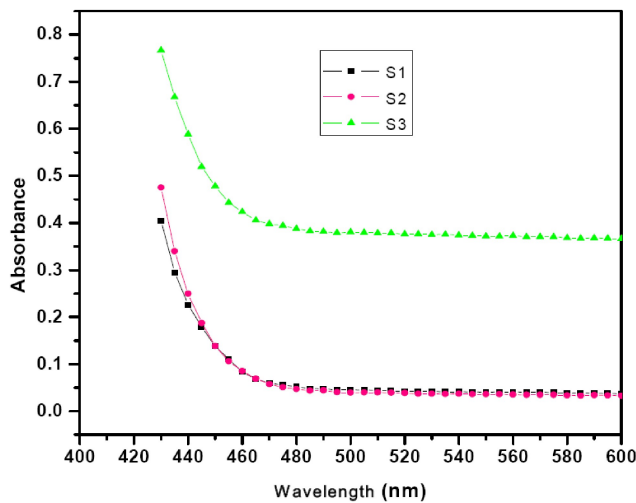

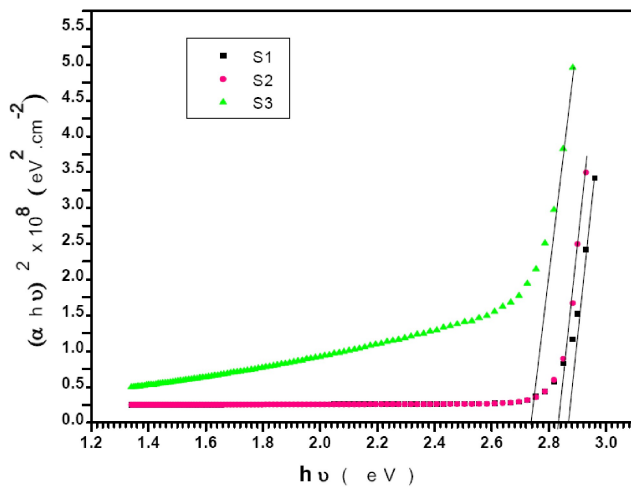**Figure 2 : The variation of optical absorbance vs. wavelength for Znse films**

Figure 3 : The variation of $(\alpha h\upsilon)^2$ vs. $h\upsilon$ to determine the direct band gap of ZnSe thin films

in the as-grown ZnSe. The ZnSe film annealed at 300 °C showed the reflection peaks that correspond to hexagonal type[19] and cubic plane phase of ZnSe films. The XRD peaks of film annealed at 400 °C shows increase in intensity of direction peaks that corresponds to hexagonal phase a long with appearance of new peaks that corresponds to ZnO formed by substitution of oxygen for selenium according to the reaction

$$2ZnSe + 3O_2 \rightarrow 2\ ZnO + 2\ SeO_2 \uparrow \qquad (15)$$

The crystallite size (D) of the as deposited and the annealed films were determined for the (111) peak using the Scherrer's formulas and it was found to be increase in size with annealing temperature as shown in Figure 7. This shows that there an enhancement of a crystallite size with annealing temperature.

Electrical properties

The electrical transport properties of the materials are of great importance in determining whether the material is congruent with our necessities or not. The electrical properties are dependent on growth parameters such as film composition, thickness, substrate temperature and deposition method.
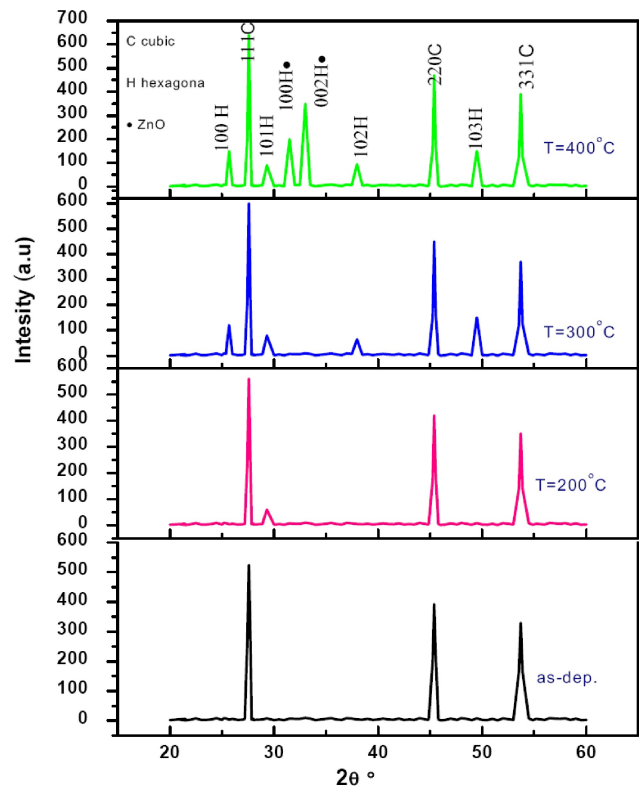

Figure 4 : XRD patterns of ZnSe thin film (S3) for different annealing temperature
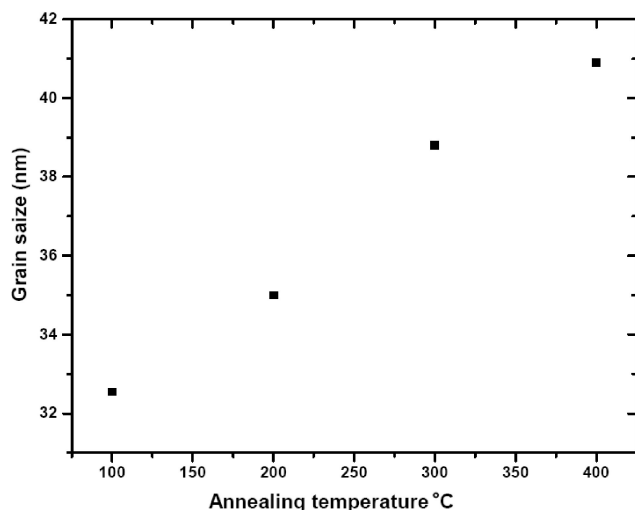
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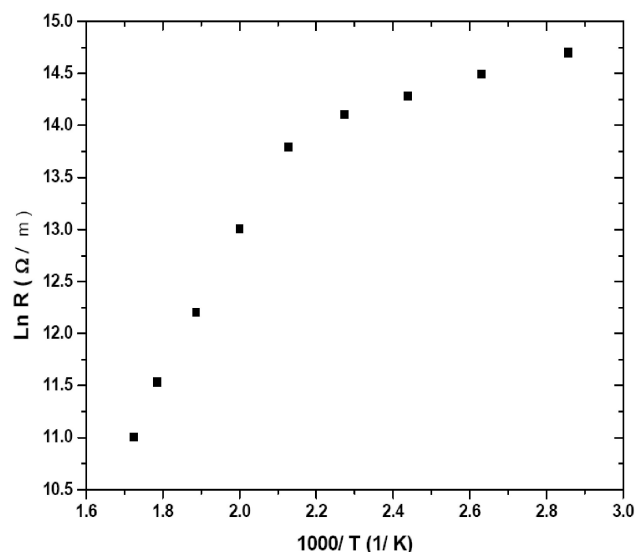**Figure 5 : Grain size of ZnSe thin films for different annealing Temperature**

Figure 6 : lnRversus 1/T graph for ZnSe thin films for different concentration of zinc acetate

The electrical resistivity of the samples was measured in the temperature range of (300- 575) K. The temperature dependence of the electrical resistivity has been plotted in Figure 5. This figure shows that the resistivity of the samples decreases with the increases temperature which is the indication of semiconductor behavior. The room temperature electrical resistivity of all the samples was of the order of $10^6 \Omega$. cm, thicker film being more resistive this high value of resistivity may be attributed due to nanocrystallinity of film, grain boundary discontinuities, and presence of surface states and small thickness of the film. The activation energy of the films was obtained using the following equation;[20]

$$R = R_0 \exp\left(-\frac{Ea}{K_\beta T}\right) \qquad (16)$$

Where R is resistivity at temperature T , R_0 is the resistivity at room temperature, E_a is the activation energy and K_β is Boltzmann constant. The activation energy represents the location of trap levels below the conduction band. Fig. 6 shows the plots of ln R versus 1000/T. The slope of a straight line gives the activation energy (Ea) and intercepts lnR. It can be observed from figure 6 that there are two distinct regions. The first, in the lower temperature range ($\Delta T = 300-434$ K) is characterized by a smaller slope and higher temperature range ($\Delta T= 434-575$ K) the curve is characterized by larger slope. This indicated two types of conductivity mechanism for the carrier transport in ZnSe films in the low and high temperature regions. The activation energies are 0.085 and 0.6 eV for low and high temperature region, respectively. These activation energies correspond to a shallow donor level and deep acceptor one, as proposed by Bube[21]. This results are very good agreement with the data reported by (kale and lokhande, 2004)[8].

CONCLUSIONS

ZnSe thin films have been successfully synthesized by chemical bath deposition and the effect of concentration of Zinc acetate of the bath on structural, optical and electrical properties are studied. XRD study revealed polycrystalline nature of the films with cubic phase. With increasing annealing temperature from 200 to 400 ºC the films developed tendency to adopt predominantly hexagonal structure. Various structured parameters are calculated. Optical absorption study revealed direct band nature. Their optical band gap showed a blue shift because of quantum size effect. The room temperature electrical resistivity of all the samples lies in the range of 4.4–0.7 Ω-cm.

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