Effect of substrate temperature on structural properties of thermally evaporated ZnSe thin films

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The ZnSe, a wide band gap semiconductor has high potential for application in optoelectronic applications. The structural parameters of a thin film semiconductor largely depend on the preparation method and condition. Transparent ZnSe thin films of thicknesses from 2000 Å to 4500 Å have been prepared by thermal evaporation method on chemically cleaned glass substrates at different substrate temperatures from 300K to 573K. The film structure was studied by X-ray diffraction technique and different micro structural parameters were determined from it. The ZnSe films prepared at higher substrate temperature have been polycrystalline in nature and have a cubic (zinc-blende) structure. The average grain size and average internal strain of these films were calculated from the broadening of the XRD line spectra by plotting Williamson and Hall plots. The grain size of the polycrystalline ZnSe film was found to increase from 160 Å to 454 Å with increase of substrate temperature from 373K to 573K. The internal strain and dislocation density of these films were found to decrease with increase of substrate temperature and also with thickness.

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1. Introduction

ZnSe(Zinc-Selenide), a direct gap II-VI semiconductor with band gap energy of 2.67 eV, has long been found as promising material for optoelectronic devices such as LED, thin film transistor, blue laser diode etc [1-3]. Because of its large band gap, ZnSe has been used as window layer for the fabrication of photovoltaic solar cells. There are a number of reports on the different structural, optical and electrical properties of ZnSe polycrystalline thin films prepared by various techniques such as Chemical vapour deposition, MOCVD, Electrodeposition, Photochemical deposition, Chemical bath deposition(CBD), Pulsed laser deposition and thermal evaporation [4-12]. It is seen that different parameters of a film are structural dependent which is also depended on the method of preparation, its thickness and other factors. Also the mechanical stability of the thin film is one of the major factors for designing various optoelectronic devices. The thermal evaporation method is cost effective and suitable for large area deposition. We have prepared ZnSe thin films of different thicknesses by thermal evaporation method at different substrate temperatures and the different microstructural parameters of these films were determined from their XRD spectra. In the present work, the effect of substrate temperature and thickness of thermally deposited ZnSe films is investigated to optimize the growth condition for a good quality film which will be suitable for optoelectronic devices.

2. Experimental

The ZnSe films were prepared by vacuum evaporation method under the pressure better than 10^{-5} Torr on chemically cleaned glass substrates from 99.99% pure ZnSe powder (Aldrich) using molybdenum boat. The substrates were kept at a distance 8 cm from the material boat. The ZnSe films of different thicknesses in the range 2000–4500 Å were deposited at a nearly same deposition rate at different substrate temperatures from 373 K to 573 K for different sets of films. After deposition, each set of films were vacuum annealed in-situ at 373K for one hour. The thickness of all the films was measured by multiple beam interferometer (MBI) technique. In order to study the structural properties the films were analyzed by an X-ray diffractometer (D8 Advance, Bruker) using CuK_α radiation with wave length (λ) 1.5406 Å in the 2θ range from 10^0 to 70^0. Surface morphological studies of the thermally deposited ZnSe thin films were done using the Scanning Electron Microscope (LEO 1430 VP) operating with an accelerating voltage 15 kV. The quantitative compositional analysis of the ZnSe films were carried out by EDAX (Energy dispersive X-ray Analyzer) attached with the SEM.

3. Results and discussions

3.1 Structural analysis

3.1.1 X-ray diffractograms

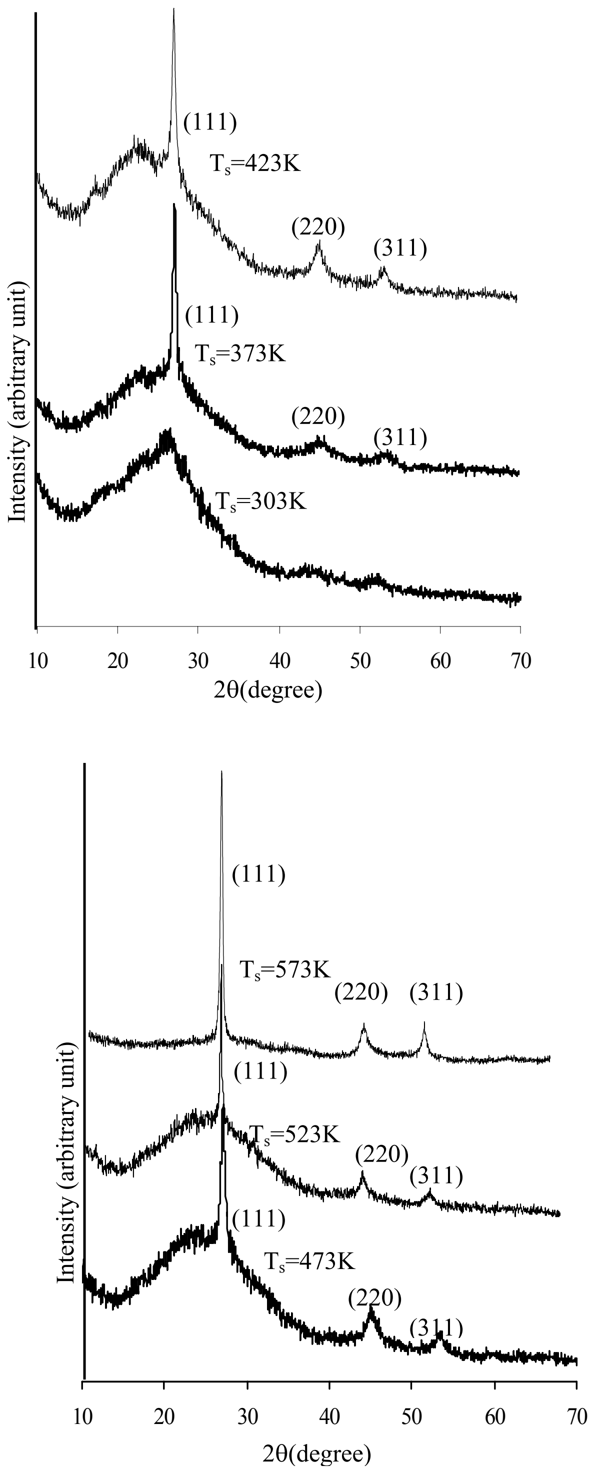

Fig. 1. XRD spectra of six typical ZnSe films (annealed) of thickness about 3000 Å thermally deposited at different substrate temperatures (T_s)

X-ray diffractograms of the ZnSe films of thickness in the range of 2800Å to 3200Å deposited at different substrate temperatures are shown in the Figure 1. From the XRD patterns it is found that the ZnSe films prepared at room temperature is amorphous in nature. As the substrate temperature is increased the films becomes polycrystalline. The main features of the diffraction pattern are the same but only the peak intensity is varied. The X-ray diffraction of thinner films shows almost featureless spectra with very weak peaks. The peak intensity increases with increasing film thickness. The diffraction spectra display the characteristics diffraction peaks of the cubic phase of ZnSe with zincblende structure [13]. Three prominent diffraction peaks at 2θ values at 27.224, 45.23 and 53.649 degree correspond to (111), (220) and (311) planes and indicate a preferential orientation along the [1 1 1] direction. The [111] is the close packing direction of zinc blende structure. It is also observed that with increasing substrate temperature, the peak intensity (counts/sec) increases and the peaks become sharper indicating larger crystallite size D at elevated substrate temperature. From these results it can be concluded that the elevated substrate temperatures (373 K to 573 K) are the suitable optimum growth conditions to prepare good quality polycrystalline thin films. As the film thickness increases, the diffraction intensity increases due to the growth of the materials incorporated in the diffraction process [14].

3.1.2 Lattice parameters

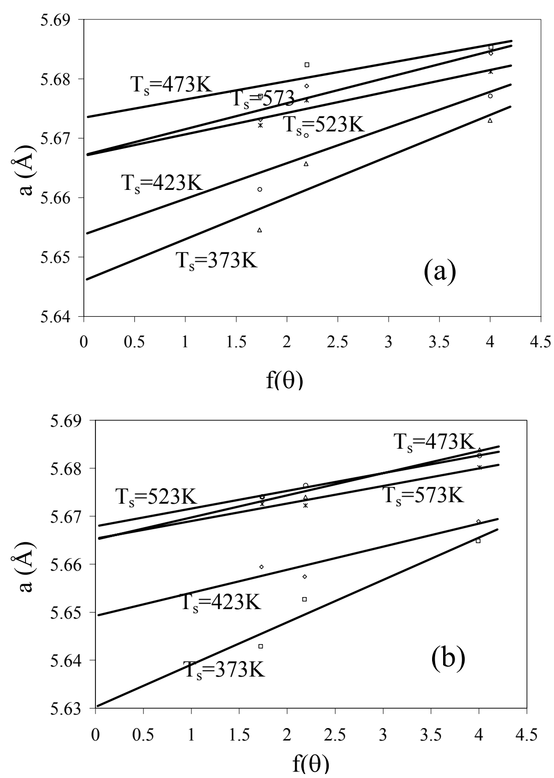

Fig. 2. Nelson-Riley plots for calculation of corrected value of lattice constant of ZnSe films deposited at different substrate temperatures of thickness (a) about 2100 Å and (b) about 3000 Å.

The lattice constants of all the ZnSe thin films prepared at different substrate temperatures on glass substrates for the cubic structure were determined from the relation $a=d(h^2+k^2+l^2)$, and have been tabulated in Table1. The lattice constant is found to be slightly different for different orientations of the same film. This is due to divergence of the X-ray beams, refraction and absorption of X-rays by the specimens etc., which give error in the measurement of θ and hence in the d values. From the calculated values of lattice constants (a) for different planes we have drawn Nelson–Riley plots [15] (Figure 2) with error function $f(\theta)=\frac{1}{2}\left(\cos^2\theta/\sin\theta+\cos^2\theta/\theta\right)$. The corrected values of lattice constants are estimated from the intercept of the curve for error function, at $f(\theta)=0$. The corrected values of lattice constants found for each film is tabulated in Table1. The variation of lattice constant (corrected) with substrate temperature is shown in figure 3. From the plot it is seen that the lattice constant first increases with substrate temperature and reaches nearer to the value of lattice constant of bulk ZnSe (5.667 Å) at substrate temperature in between 473K and 523K and then shows a decreasing tendency.

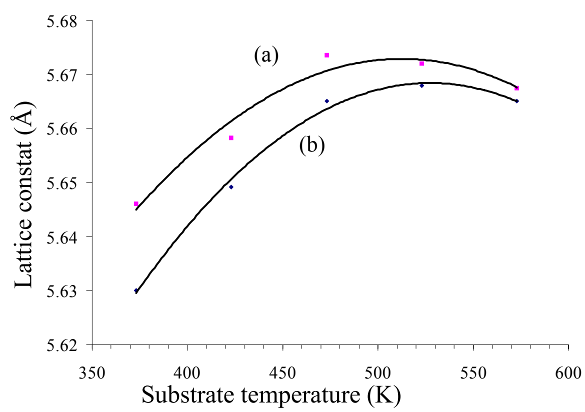

Fig. 3. Variation of lattice constant (corrected) with substrate temperature of ZnSe films of thickness (a) about 2100 Å (b) about 3000 Å

3.1.3 Average grain size and internal strain measured from W-H plot

In the thin film samples, the broadening of X-ray diffraction peaks arises due to the presence of stress and strain also. Considering the entire broadening of diffraction profile to be due to simultaneous contributions from both particle size and strain and using the Williamson and Hall method [16] for Cauchy nature of broadened profile, we have the relation [17],

$$\beta=\frac{\lambda}{D\cos\theta}+4\varepsilon\tan\theta$$

$$\text{or, } \frac{\beta\cos\theta}{\lambda}=\frac{1}{D}+4\varepsilon\frac{\sin\theta}{\lambda}$$

For the multiple ordered diffraction pattern, a plot of $\frac{\beta\cos\theta}{\lambda}$ versus $\frac{2\sin\theta}{\lambda}$ will give a straight line and the intercept and slope of this plot (Williamson and Hall plot) will give the average grain size and average strain respectively [18].

The FWHM (Full Width at Half of the Maxima) for each diffraction peak of all the films prepared at different substrate temperatures were measured. Using the corrected value of full width at half maximum (β) of the fitted diffraction peak by subtracting instrumental broadening from the experimental integral width, $\frac{\beta\cos\theta}{\lambda}$ versus $\frac{2\sin\theta}{\lambda}$ plots were drawn for each film (Figure 4). The average grain size (D) and average strain (ε) calculated from the intercept and slope of these linear plots for different films are given in table 1. Figure 5 shows the variation of average grain size of the prepared films with substrate temperature for two ranges of thickness.

The average internal strain of the film prepared at 373K is found 3.6×10^{-3} which is reduced to 1.25×10^{-3} for the film prepared at 573K. Figure 6 shows the variation of average micro strain of the films of different thicknesses with the substrate temperature.

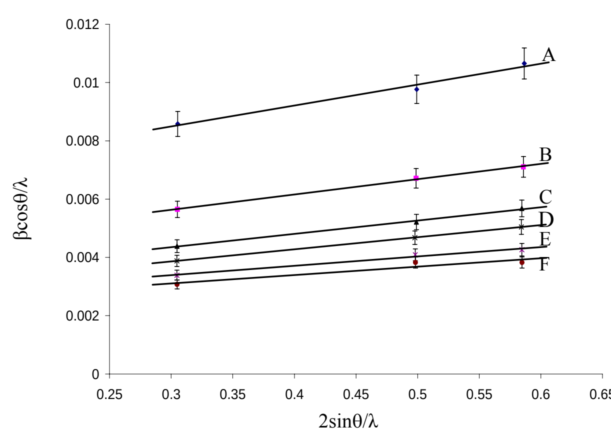

Fig. 4: W-H plots of ZnSe films of thickness about 3000 Å deposited at substrate temperature (A) 373K, (B) 423K, (C) 453K, (D) 473K, (E) 523K and (F) 573K

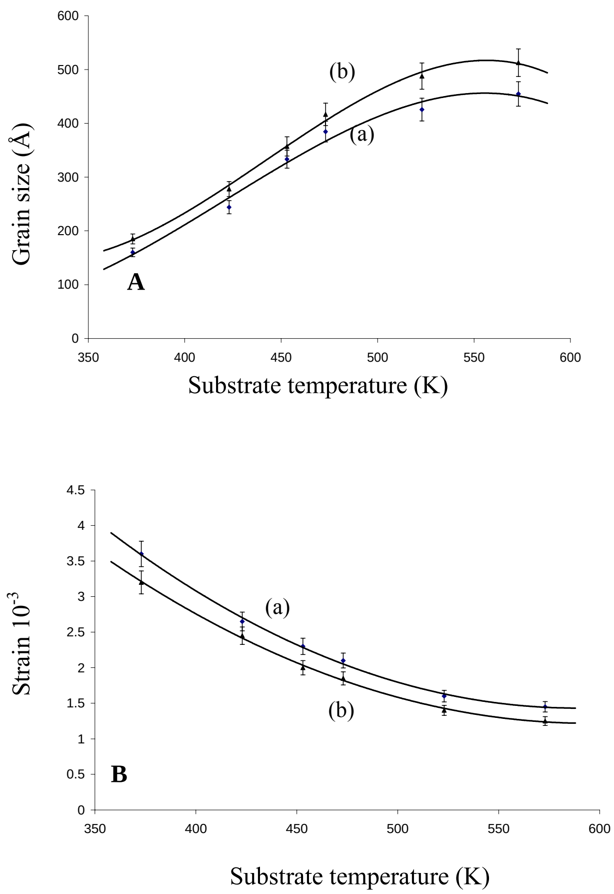

Fig. 5. Variation of (A) average grain size and (B) average strain with substrate temperature of ZnSe films of thickness (a) about 2100 Å (b) about 3000 Å.

3.1.4 Internal stress

A stress is always developed in all vacuum deposited films due to the lattice misfit with the substrate. However, the stress has two components: thermal stress arising from the difference of expansion coefficient of the film and substrate and internal stress due to the accumulating effect of the crystallographic flaws that are built into the film during deposition. All the evaporated films are found to be dominated by internal stress rather than thermal stress [18]. The average internal stress developed in the films is calculated by using the relation [19], $S = \frac{E}{2\gamma}\frac{(a-a_0)}{a_0}$ from the observed value of lattice constant. In the calculation, standard value of lattice constant (a_0 =5.667Å), Young's modulus (E =67.2×10^9 dyne/cm^2) and Poisson's ratio (γ=0.28) for bulk material are used. The negative value of average stress indicates the compressive stress and the positive sign of the stress indicates the tensile stress [20]. From the table 5.03, it is seen that most of the ZnSe films deposited below 473K possess compressional stress. Similar behaviour was observed by other workers on physical vapour deposited ZnSe films [29-23]. From figure 6, it is seen that the compressional stress decreases with increase of substrate temperature and changed to tensile stress at the substrate temperatures 473K.

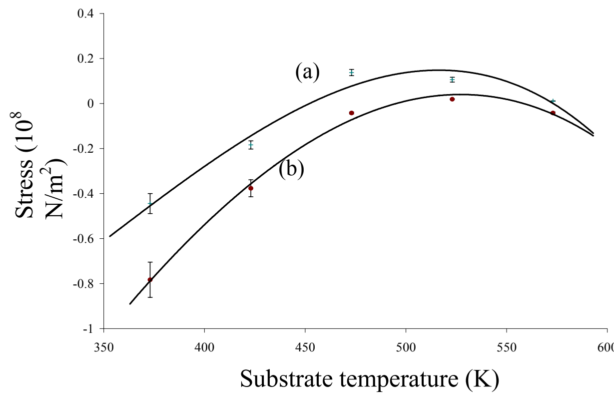

Fig. 6. Variation of average stress with substrate temperature of ZnSe films of thickness (a) about 2100 Å (b) about 3000 Å

3.1.5 Dislocation density

The dislocation density (*δ*), defined as the length of dislocation lines per unit volume of the crystal, can be evaluated from the formula [23] $\delta_{hkl} = m\varepsilon/aD$. The average dislocation density of ZnSe thin films for the preferred orientation was calculated making use of the values of grain size, average microstrain, lattice constants and the value of constant m as15 for (111) plane [24]. The estimated dislocation densities for the films prepared at different temperatures are tabulated in table1 and presented by figure 7. It is seen that the dislocation density decreases abruptly with increase of substrate temperature upto 473K and then decreases slowly.

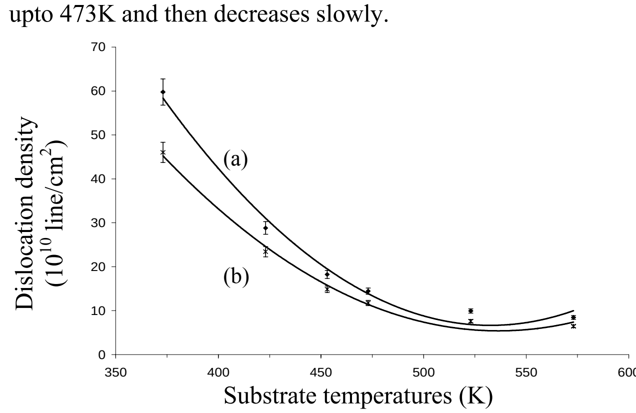

Fig. 7. Variation of lattice dislocation density with substrate temperature of ZnSe films of thickness (a) about 2100 Å (b) about 3000 Å

Table 1. Microstructural parameters of thermally evaporated ZnSe thin films of different thicknesses prepared on glass substrate at different substrate temperatures.

Substrate temperature K	Thickness (Å)	Plane (hkl)	Lattice constant (Å)	Corrected Lattice constant (Å)	Average Grain Size (Å)	Average Internal stress $10^8 N/m^2$	Average Internal strain 10^{-3}	Dislocation density 10^{10}line/cm^2
373	2000	(111) (220) (311)	5.673 5.6657 5.6545	5.646	160	-4.447	3.60	59.77
	2800	(111) (220) (311)	5.665 5.653 5.643	5.63	185	-7.835	3.2	46.04
423	2100	(111) (220) (311)	5.677 5.670 5.661	5.6583	244	-1.842	2.65	28.80
	3100	(111) (220) (311)	5.669 5.657 5.659	5.65	278	-3.769	2.45	14.87
473	1900	(111) (220) (311)	5.685 5.682 5.677	5.6735	385	+1.376	2.10	14.43
	3200	(111) (220) (311)	5.684 5.674 5.674	5.665	417	-0.423	1.85	11.75
523	1800	(111) (220) (311)	5.684 5.678 5.673	5.672	425	+1.058	1.60	9.940
	2900	(111) (220) (311)	5.682 5.676 5.674	5.668	488	+0.190	1.40	7.595
573	2200	(111) (220) (311)	5.681 5.676 5.672	5.6675	454	+0.106	1.45	8.443
	3000	(111) (220) (311)	5.68 5.672 5.672	5.665	513	-0.423	1.25	6.454

Table 1 shows a comparative look of grain size, internal stress, internal strain and dislocation density of the ZnSe thin films of different thicknesses prepared on glass substrates at different substrate temperatures.

It is observed that with increase of substrate temperature, the crystallite size increases but the internal strain and dislocation density decreases. When thickness increases the average grain size increases. Since the dislocation density and strain are the manifestation of dislocation network in the films, the decrease in the dislocation density and strain indicates the formation of higher quality films at higher substrate temperatures. In most of the films the average stresses of the deposited films are found to be compressional in nature as reported earlier [21-24]. The compressive stress is due to the grain boundary effect, which is predominant in polycrystalline film [25]. When the substrate temperature is increased, the line width narrows, and the value of FWHM decreases. This indicates the decrease in the concentration of lattice imperfections due to the decrease in the internal micro-strain within the films and an increase in the crystallite size [14]. The adatom mobility also increases as the substrate temperature increases which also contributes to the crystallinity of the films [26].

3.2 Morphological and quantitative study

3.2.1 Scanning electron microscopy

Fig. 8 show the scanning electron micrograph of a typical ZnSe thin film of thickness 1900Å deposited at a substrate temperatures of 473K. The film morphology under SEM studies show that the films deposited at higher substrate temperature are fairly uniform and polycrystalline; and the film well covers the glass surface. The grain sizes in the films are seen to be almost uniform. There are no macroscopic defects like void, pinhole, peeling or cracks. From the featureless surface morphology we can anticipate that these films will exhibit very low optical scattering losses and should therefore be suitable for optoelectronic applications.

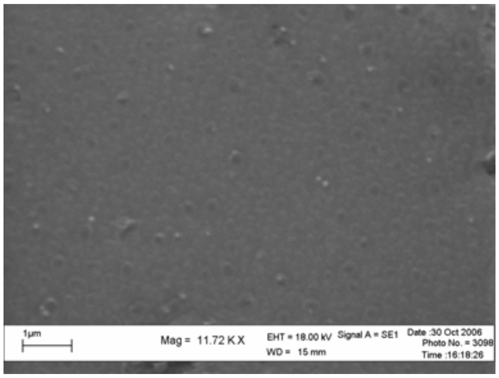

Fig. 8. SEM photograph of ZnSe thin film of thickness 1900Å deposited at T_s=473 K

3.2.2 Composition analysis

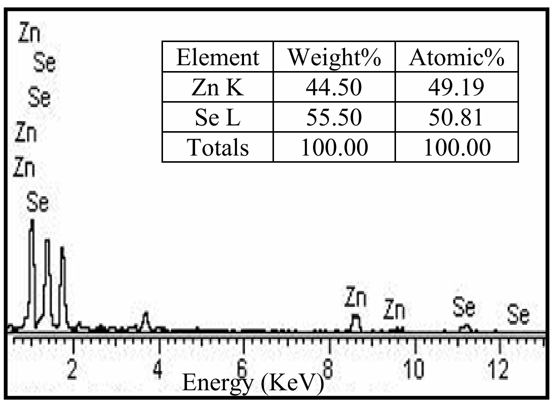

Fig. 9. The EDAX spectrum giving the compositional information of ZnSe film deposited at 473 K.

From the EDAX spectra, it is found that the thermally deposited ZnSe films contain only Zinc and Selenium, no peaks were found for any impurity. Typical EDAX results showing the atomic contents of elements present in some of the ZnSe film deposited at substrate temperature 473 K is presented in Fig. 9. The film prepared at lower substrate temperature is found to be Zn deficient as reported by other workers [21], because the vapour pressure of Se is greater than that of Zn and their sticking coefficients are also different. For the ZnSe film thermally deposited at substrate temperature 473 K, the average atomic percentage of Zn and Se is found to be 49.2 and 50.8, showing that the film is almost stoichiometric.

4. Conclusions

Uniform ZnSe thin films without any macroscopic defects were prepared on glass substrates by thermal evaporation method at elevated substrate temperatures. From the XRD spectra of the thermally deposited ZnSe films, it is found that the films prepared within substrate temperature range 373 K to 573 K are polycrystalline in nature and have a cubic (zinc-blende) structure. The different structural parameters such as crystalline size, lattice constant, stress, strain and dislocation density of prepared films were calculated from their XRD spectra. With the increase of substrate temperature the average grain size of the films is found to be increased, however the internal strain and dislocation density decreased. At a substrate temperature of about 500 K, good quality and nearly stoichiometric thin films of ZnSe can be deposited at which the lattice constant is found to be nearer the value of bulk ZnSe.

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