

Structural characterization of vacuum evaporated ZnSe thin films

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Abstract. Thermally evaporated ZnSe thin films deposited on glass substrates within substrate temperatures (T_s) at 303 K–623 K are of polycrystalline nature having f.c.c. zincblende structure. The most preferential orientation is along [111] direction for all deposited films together with other abundant planes [220] and [311]. The lattice parameter, grain size, average internal stress, microstrain, dislocation density and degree of preferred orientation in the film are calculated and correlated with T_s .

Keywords. ZnSe thin films; X-ray diffraction; average internal stress; microstrain; dislocation density.

1. Introduction

Thin films of ZnSe has attracted considerable interest over the years owing to their wide range of applications in various opto-electronic devices and in solar cells (Siche and Hatmann 1996; Tafreshi *et al* 1997). It has a direct band gap (2.67 eV) and transparent over a wide range of visible spectrum. More progress has been achieved in fabrication of blue-green light emitting diodes, dielectric mirrors, filters and other optically sensitive devices (Schmidt *et al* 1990; Wang *et al* 1992). It is seen that the photoelectronic and other properties of II–VI class of compound thin films are highly structure sensitive which in turn can severely influence the device performance. The structure parameters viz. the crystallinity, crystal phase, lattice constant, average stress and strain, grain size, orientation etc are strongly dependent on deposition parameters. The structure of thermally evaporated ZnSe thin films are likely to be governed by the rate of deposition, substrate temperature, composition and film thickness. Although many investigations on ZnSe thin films have been done so far (Chaudhuri *et al* 1992; Lakshmikummar and Rastogi 1995; Sherif *et al* 1996), it is felt that little attention is given on their structural characterization and their correlation to other properties. Keeping in view all these aspects, an experimental study on the structural characterization of thermally evaporated ZnSe thin films has been undertaken. A correlation between substrate temperatures and different structural parameters has been highlighted in this paper.

2. Experimental

ZnSe thin films were deposited on highly clean glass substrates in a vacuum better than 10^{-6} torr by using thermal

evaporation method (HINDHIVAC 12A4). Specpure ZnSe powder (99.999%) procured from Koch Light Lab., UK was used for deposition. Thin films were deposited within substrate temperature range (303 K–623 K). The rate of deposition was 2.5 Å/sec and the source to substrate distance was kept at 6 cm in all cases. The thickness of the films was measured by using the multiple beam interferometry method. The accuracy of thickness measurements was ± 20 Å. The X-ray diffraction (XRD) patterns of the deposited films were recorded with the help of Philips (PW 1830) X-ray diffractometer using $\text{CuK}\alpha$ radiation. The tube was operated at 30 KV, 20 mA with the scanning speed of 0.030 (2θ)/sec. The XRD patterns of all films were taken from 10° to 70° (2θ). The peaks of the XRD patterns were searched by computer programming using Savitzky and Golay (1964) method.

3. Determination of structural parameters

3.1 Lattice constant

The vacuum evaporated ZnSe thin films possess cubic zincblende structure. It is confirmed by comparing the peak positions (2θ) of the XRD patterns of the films with the standard X-ray powder diffraction data file (card no. 5-522). The lattice constant 'a' for the cubic phase structure is determined by the relation

$$a = d/\sqrt{(h^2 + k^2 + l^2)}.$$

The corrected values of lattice constants are estimated from the Nelson–Riley plots (figure 2a). The Nelson–Riley curve is plotted between the calculated 'a' for different planes and the error function

$$f(\theta) = 1/2 (\cos^2\theta/\sin\theta + \cos^2\theta/\theta).$$

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3.2 Average internal stress and microstrain

Thornton and Hoffmann (1989) revealed that all vacuum evaporated films are in a state of stress. The total stress is composed of a thermal stress and an intrinsic stress. The thermal stress is due to the difference in the thermal expansion coefficients of the film and substrate material. The intrinsic stress is due to the accumulating effect of the crystallographic flaws that are built in the film during deposition. It is difficult to avoid thermal stress for film deposited at any temperature. In the present case the thermal stress developed in the films, deposited even at ~ 623 K is found to be 5% of total stress. Therefore it is believed that for high melting material like ZnSe, the internal stress accumulates and tends to dominate over thermal stress. The average internal stress developed in the films is determined by the relation (Chopra 1969),

$$S = (E/2\gamma) (a_0 - a)/a_0.$$

Here E and γ are the Young's modulus and Poisson's ratio of ZnSe film. Standard bulk values of E and γ are used (Hearman 1969) in calculation of stress. a_0 is the bulk lattice constant of ZnSe. The estimated 'a' refers to the lattice constant perpendicular to the film plane.

The origin of the strain is also related to the lattice misfit which in turn depend upon the deposition conditions. The microstrain (ϵ) developed in the ZnSe film is calculated from the relation

$$\epsilon = (\beta_{2\theta} \cos \theta)/4,$$

where $\beta_{2\theta}$ is the full width at half maximum of [111] peak.

3.3 Grain size

It is observed that the XRD patterns of all ZnSe thin films show a most preferred orientation along [111] plane. The [111] direction is the close-packing direction of the zincblende structure. The grain size of the deposited films is estimated using Scherrer formula (Warren 1969),

$$D = k\lambda/\beta_{2\theta} \cos \theta.$$

Here k is taken as 0.94, λ the wavelength of X-ray used and $\beta_{2\theta}$ the full width at half maximum of [111] peak of XRD pattern.

3.4 Dislocation density

A dislocation is an imperfection in a crystal associated with the misregistry of the lattice in one part of the crystal with that in another part. Unlike vacancies and interstitial atoms, dislocations are not equilibrium imperfections, i.e. thermodynamic considerations are insufficient to account for their existence in the observed densities. In fact, the growth mechanism involving dislocation is a matter of importance. In the present study, the dislocation density is

estimated from Williamson and Smallman method using the relation (De and Mishra 1997)

$$\rho = 15\epsilon/aD,$$

for cubic ZnSe thin films.

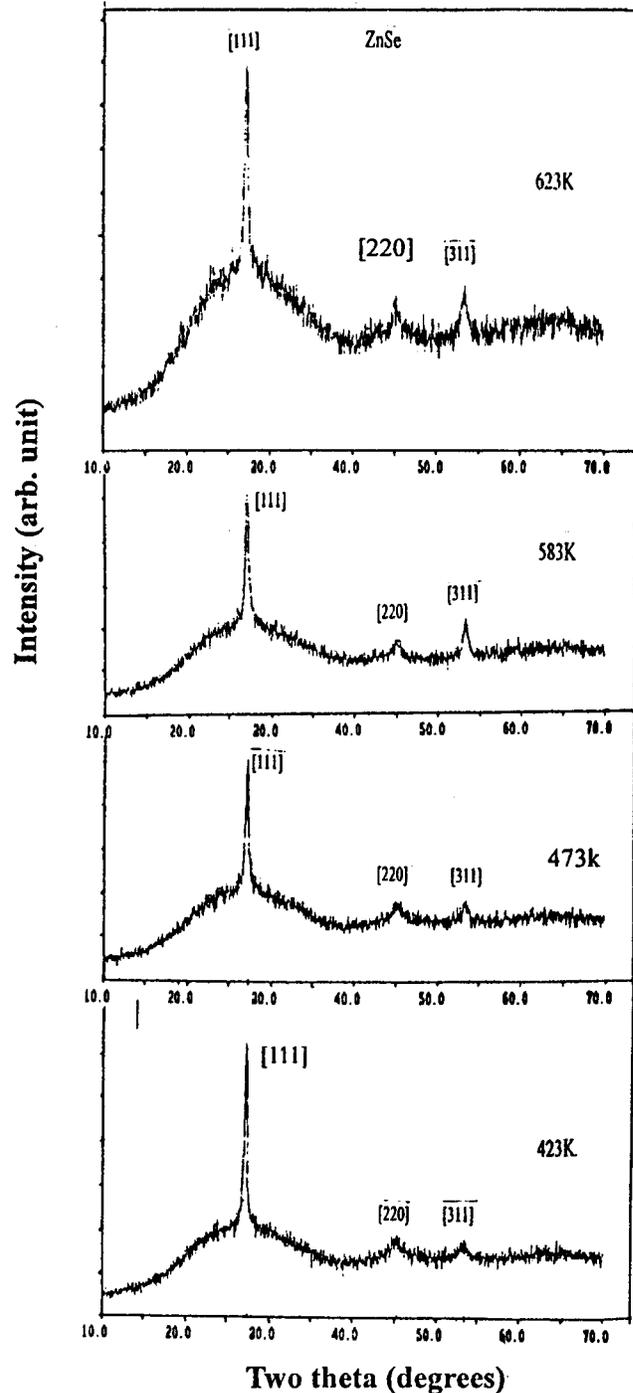


Figure 1. XRD traces for representative ZnSe films having thickness 2000 Å and deposited within substrate temperature range (423 K to 623 K).

Table 1. Structural parameters of thermally evaporated ZnSe thin films having thickness 2000 Å.

| T_s (K) $t = 2000$ Å | 2θ (degrees) | d (Å) | $[hkl]$ | a calculated (Å) | a corrected (Å) | D (Å) | $S \times 10^9$ (dy/cm ²) | $\epsilon \times 10^{-3}$ | $\rho \times 10^{11}$ /cm ² |
|---------------------------|------------------------|------------|---------|-----------------------|----------------------|------------|--|---------------------------|--|
| 423 | 27.1475 | 3.2821 | [111] | 5.6847 | 5.6815 | 180 | -2.43 | 1.99 | 2.90 |
| | 45.1625 | 2.0060 | [220] | 5.6738 | | | | | |
| | 53.3575 | 1.7153 | [311] | 5.6890 | | | | | |
| 473 | 27.1225 | 3.2851 | [111] | 5.6899 | 5.7074 | 170 | -8.45 | 2.16 | 3.39 |
| | 44.9975 | 2.0130 | [220] | 5.6936 | | | | | |
| | 53.2325 | 1.7194 | [311] | 5.7026 | | | | | |
| 583 | 27.0950 | 3.2883 | [111] | 5.6955 | 5.6821 | 180 | -2.57 | 1.99 | 2.90 |
| | 45.0625 | 2.0102 | [220] | 5.6857 | | | | | |
| | 53.3550 | 1.7157 | [311] | 5.6903 | | | | | |
| 623 | 27.1225 | 3.2851 | [111] | 5.6899 | 5.6764 | 200 | -1.25 | 1.78 | 2.31 |
| | 45.2300 | 2.0032 | [220] | 5.6659 | | | | | |
| | 53.3175 | 1.7168 | [311] | 5.6939 | | | | | |

4. Results and discussion

It is observed that all ZnSe thin films are polycrystalline having f.c.c. zincblende structure irrespective of their substrate temperature and thickness. Figure 1 represents the XRD patterns of four representative ZnSe thin films having thickness 2000 Å and deposited within the substrate temperature at 423 K to 623 K. All films show the most preferred plane [111] in addition to other [220] and [311] prominent reflections. No other peak beside these is observed which establishes the single phase cubic structure of the films.

The various structural parameters for ZnSe thin films deposited at different T_s are calculated using the relevant formulas and are systematically represented in table 1. The lattice parameter, average internal stress, microstrain, dislocation density and degree of preferred orientation are correlated with T_s which is depicted in figure 3. The correct values of lattice constants are estimated from the Nelson–Riley plots (figure 2a) which are found to be within the range of 5.6764 Å to 5.7074 Å. The lattice constant 'a' first increases and reaches maximum around 473 K and then shows a decreasing tendency with substrate temperature (figure 2b). The change in lattice constant for the deposited thin film over the bulk clearly suggests that the film grains are strained and that may be owing to the change of nature and concentration of the native imperfections. The density of film is therefore expected to change in accordance with the change of lattice constant (Reichelt and Jiang 1990; Sherif *et al* 1996). The grain size of the deposited films are small and are within the range of 170 Å to 200 Å. The change of grain size with T_s is not very prominent.

The average internal stress for the ZnSe film deposited at high substrate temperature (figure 3a) is found to be compressional in nature. Compressive stress is also likely due to the native defects arising from the lattice misfit.

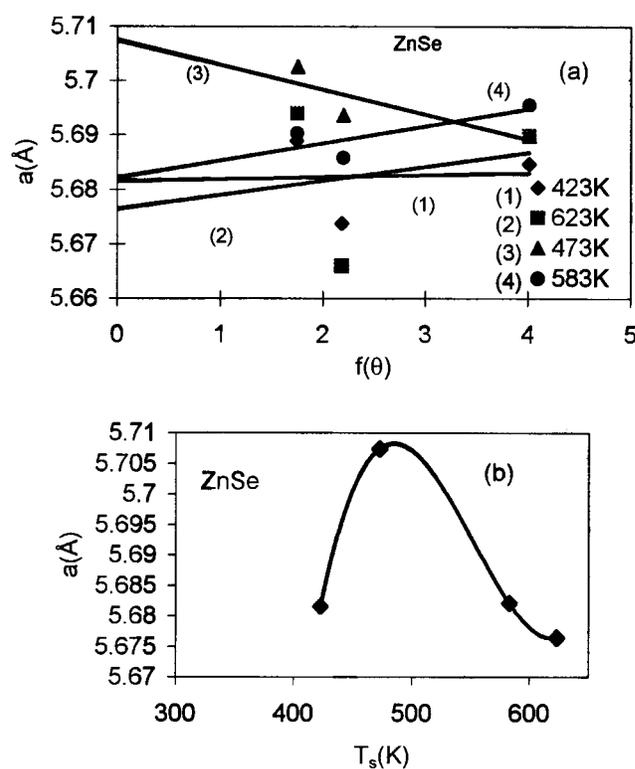


Figure 2. a. Nelson–Riley plots for accurate measurement of lattice constants of ZnSe films and b. variation of lattice constant with substrate temperature (T_s).

The defects have a probability to migrate parallel to the film surface with the surface mobility modified by the substrate temperatures so that the films have a tendency to expand and develop an internal compressive stress. The stress increases up to 473 K and then shows a decreasing trend at higher substrate temperature. This type of change in intrinsic stress may be due to the predominant recrystallization process in the polycrystalline films. The stress

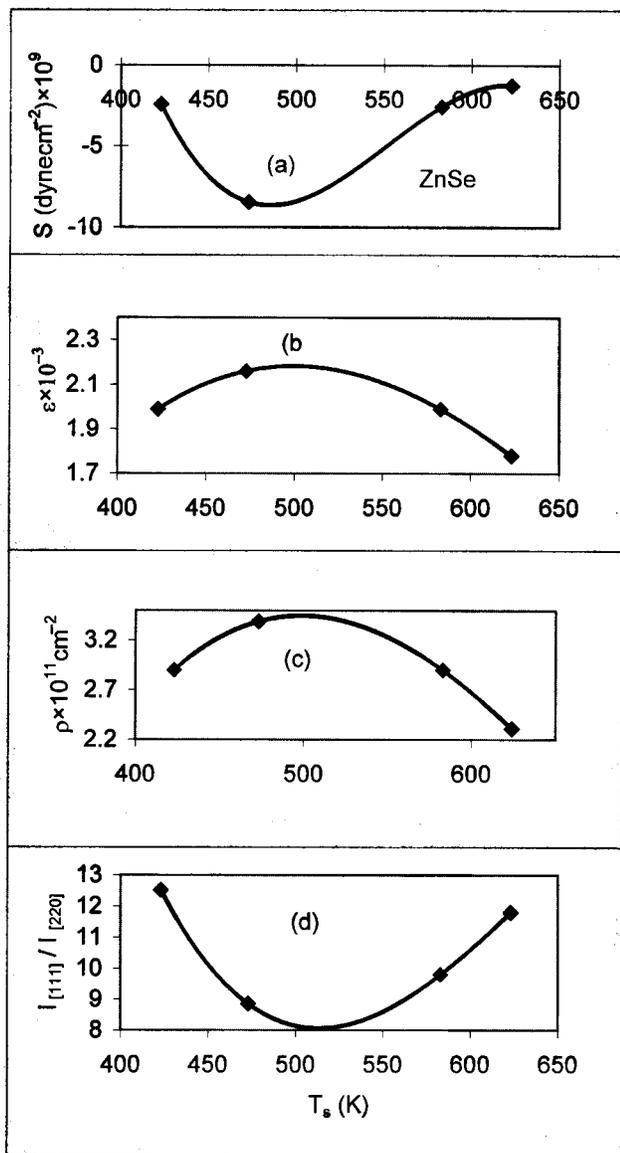


Figure 3. Variation of (a) average internal stress S , (b) microstrain ϵ , (c) dislocation density ρ and (d) degree of preferred orientation with T_s in ZnSe films (2000 Å).

relaxation is mainly considered due to dislocation glides formed in the films. The decrease of average internal stress beyond 473 K may correspond to a decrease in dislocation density. It is observed that microstrain (ϵ) and dislocation density (ρ) exhibit a slow increasing trend up to about 473 K and afterwards decrease with higher T_s (figures 3b and c). The decrease of ϵ and ρ at high substrate temperatures may be due to the movement of interstitial Zn atoms from inside the crystallites to its grain boundary which dissipate leading to reduction in the concentration of lattice imperfections.

The degree of preferred orientation in cubic ZnSe thin films can be assessed by the ratio of peak intensity of

[111] to that of [220] reflection on the same scale. Figure 3 shows that the degree of preferred orientation of the crystallites decreases when the average internal stress, microstrain and dislocation density is more and *vice versa*. This suggests that the degree of preferred orientation indeed may provide the essential characterization of inherent defect states. An increase in the degree of preferred orientation for $T_s > 473$ K (figure 3d) may therefore be expected to enhance the reduction mechanism of the imperfections originating from lattice misfit in the films. A review of dependence of above structural parameters on the substrate temperature indicates that the degree of preferred orientation along with the other microstructural features are more effective than the crystallite size for low thickness films. This type of correlation is suggested recently by other workers (Ashor *et al* 1996; El-Kadry *et al* 1996) in II–VI thin films.

5. Conclusions

All thermally evaporated ZnSe thin films of thickness 2000 Å deposited within substrate temperature range (303 K–623 K) are polycrystalline having f.c.c. zincblende type structure. Each film shows a preferred orientation along [111] plane in addition to other two prominent planes [220] and [311]. The grain size of the deposited films does not have significant dependence on T_s . The average internal stress developed in the films deposited above room temperature substrates are compressional in nature which is likely to be governed by the dominant recrystallization process. However the degree of preferred orientation is expected to play a dominant role over the crystallite size in ZnSe thin films.

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