Preparation and structural characterization of ZnSe thin films by X-ray diffraction technique

C K De, N K Misra and T B Ghosh

Department of Physics and Meteorology, Indian Institute of Technology
Kharagpur-721 302, India

Abstract   : ZnSe thin films have been grown on glass substrates from ZnSe powder synthesized in the laboratory from specpure zinc and selenium using physical vapour deposition technique. The structural characterization of the bulk material and the film have been carried out by the X-ray diffraction method. Grain size of the films has been determined and found to have typical value of 23 nm for thick films. Thickness dependence of grain size of the films is also reported. Stress developed in the films is found to be tensile in nature and is of the order of 10^9 dynes/cm^2.

In recent years, a good amount of research work has been carried out in wide band gap II-VI compound semiconductors. Zinc selenide (ZnSe), a member of the group, continues to draw considerable interest because of its potential applications in optoelectronic devices namely blue-green laser, light-emitting diodes, dielectric mirrors and filters, solar cells, photoconductors and optically bistable devices [1-4]. ZnSe has cubic zinc blende type crystal structure (hexagonal wurtzite form is rare), a direct band gap of 2 67 eV and an electron mobility of 530 cm^2 V^{-1} s^{-1} at room temperature [5]. Although studies of bulk crystal are essential for understanding some of the most fundamental properties of the material, the preparation and study of high quality thin films are desirable for device applications. With an aim to investigate the effect of microstructural parameters and impurities on optical and electronic properties of ZnSe thin films, work on the preparation and characterization of pure and doped ZnSe thin films in polycrystalline form has been undertaken. Physical vapour deposition (PVD) technique has been used for deposition of films in our laboratory. In this note, the preparation of ZnSe films at room temperature (300 K) on glass substrate and the result of X-ray diffraction studies on these films are reported.

Films were grown from ZnSe powder synthesized in the laboratory from specpure (99.999%) zinc and selenium procured from M/s Johnson Matthey and Co. Ltd (London). The synthesis of bulk ZnSe is carried out in a sealed evacuated graphitized quartz ampoule

Table 1. Interplaner spacings (d_{hkl}) and relative intensities (I/I_o) of ZnSe powder prepared in the laboratory along with the standard values for different reflections

| Planes			ZnSe prepared in the laboratory		Powdered ZnSe (Standard data)	
h	k	l	d(A)	I/I_o	d(A)	I/I_o
1	1	1	3 267	100	3 272	100
2	2	0	2 002	65	2 003	70
3	1	1	1 707	35	1 709	44
4	0	0	1 417	9	1 417	9
3	3	1	1.301	11	1 300	13
4	2	2	1 158	16	1 157	15

taking measured quantities of finely powdered constituents at 1273 K The powdered ZnSe was analyzed by X-ray diffraction technique with the help of Philips X-ray diffractometer (PW 1840) using CuK$_\alpha$ radiation. The diffraction lines thus obtained from the prepared sample were in good agreement for their d-values with standard d-values [6] for pure ZnSe as shown in the Table 1.
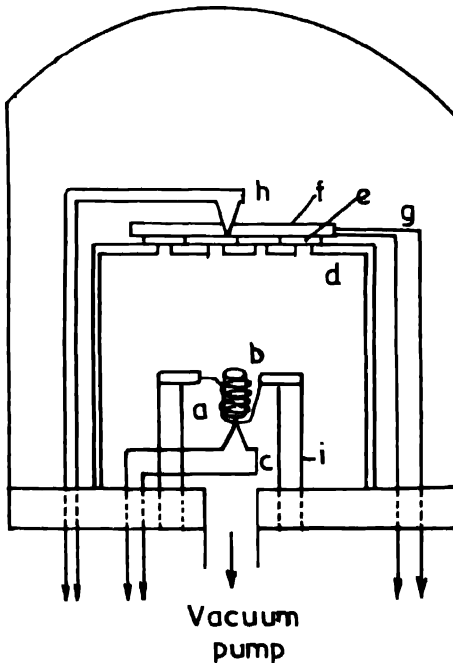
Figure 1. The layout of the film deposition system · a) tungsten wire busket; b) quartz tube; c) source thermocouple; d) substrate holder; e) substrates; f) substrate heater; g) substrate heater leads; h) substrate thermocouple; and i) source heater leads.

Films were grown on micro-glass slides of size 1.5 cm × 1.5 cm × 0.13 cm. The slides were first washed by detergent and water and then kept in chromic acid overnight. After cleaning in distilled water, the slides were washed by acetone and ethanol and dried in air. The layout of the physical vapour deposition system is shown in Figure 1. The evaporation source is a small quartz tube heated by passing current through tungsten wire basket. A chromel-alumel thermocouple lead touches the lower end of the quartz tube to measure the source temperature. The cleaned substrates are placed on an aluminium substrate holder and above the substrates is placed a mica insulated substrate heater. The substrate temperature is measured with a chromel-alumel thermocouple. The source to substrate distance in the present experiment could be varied. The films were deposited normally on the substrates at room temperature (300 K) and the source temperature was at 1143K. Typical pressure during film deposition is of the order of 10^{-6} Torr. ZnSe dissociates during evaporation according to

$$2ZnSe \rightarrow 2Zn + Se_2.$$
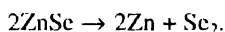
As a result, Zn and Se_2 recombine at the substrate surface to create a thin layer of zinc selenide.

The thickness of the film was measured by Form Talysurf (Taylor Hobson) by laser (HeNe, $\lambda = 640$ nm) interference with variation in the movement of a diamond tipped stylus. The resolution of the instrument is 1 nm. Structural characterization of the films were carried out by X-ray diffraction technique.
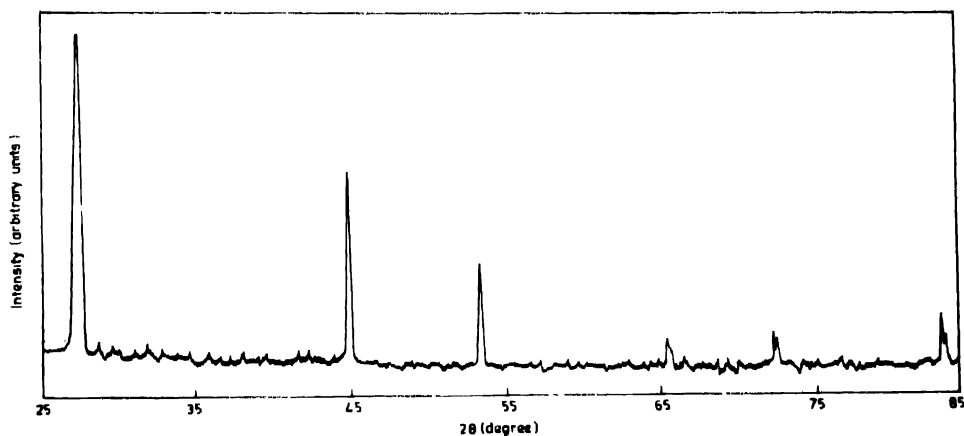

Figure 2. Diffractometer recordings ZnSe powder prepared in laboratory

The diffractometer recordings for ZnSe powder prepared and that for the films grown at 300 K on glass substrates are shown in Figure 2 and Figure 3 respectively for comparison. Whereas diffractometer recording for ZnSe powder shows peaks at $2\theta = 27.3°$, $45.3°$, $53.7°$, $65.9°$, $72.7°$ and $83.5°$, that from films on glass substrates shows a sharp peak at about $2\theta =$

27.3° only, corresponding to (111) lattice plane. This shows a preferred orientation in film growth along (111) plane. The [111] direction is the close-packing direction of the zinc blende structure. The grain size of these films was estimated using Scherrer formula [7]

$$D = K\lambda/\beta \cos\theta,$$

where K is taken as 1, λ is the wavelength of the X-ray used, β is the pure integral width of the (111) line profile Pure integral width of the (111) profiles from thin films were obtained
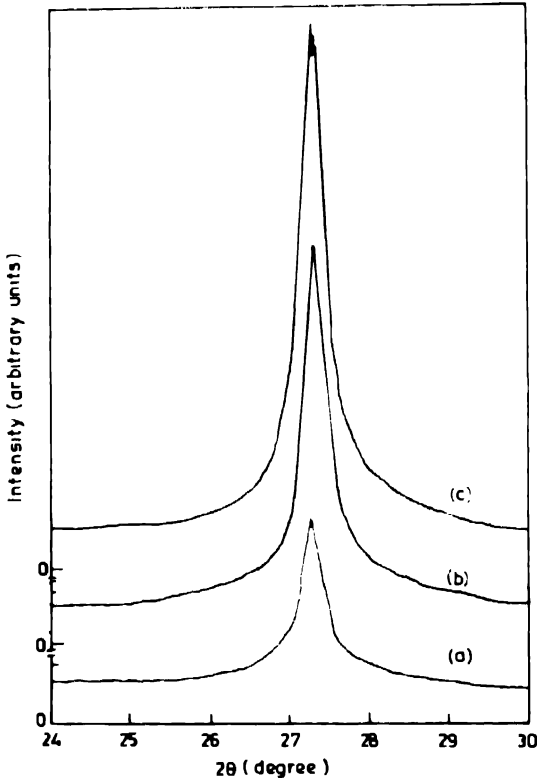

Figure 3. Line profiles of (111) peak from three films of different thickness grown on glass a) 258 nm, b) 487 nm and c) 886 nm

by subtracting geometrical integral width (b) from observed integral width (B) of the films. The geometrical integral width (b) is determined from the (111) diffraction profile of pure ZnSe powder. The grain size was also measured by Dawar *et al* [8], but they had considered the full width at half-maximum of the peak and not the integral width and also did not take care of the geometrical broadening which should be present in the observed broadening of the line profile of the films. It is observed from Table 2 that the grain size increases with film thickness but as such the values are small. The thickest film has the grain size of the order of 23 nm. It can be concluded that ZnSe films contain a large number of lattice defects even for thick ones.

The average internal stress S in the films can be determined using the following relation [9]

$$S = \left(E_f/2\gamma_f\right)(a_0 - a)/a_0$$

where a_0 and a are the lattice parameters of the bulk material and the film respectively. E_f and γ_f are the Young's modulus and Poisson's ratio of the films respectively. Here a refers to the

Table 2. Grain size (D) and average internal stress (S) of ZnSe films of different thickness

Film thickness (nm)	D (nm)	S ($\times 10^9$ dynes/cm^2)
258	17	0 2
487	20	1 4
886	23	1 4

lattice parameter perpendicular to the film plane. The values of E_f and γ_f used in calculation however are those of the bulk material [10]. Lattice parameters of the films were determined from only (111) reflection available. It is observed that the stress developed in the films is tensile in nature and is of the order of 10^9 dynes/cm^2.

Optical transmission and absorption measurements have been carried out on ZnSe films grown on glass substrates in order to determine the absorption coefficient, refractive index, extinction coefficient and band gap and their dependence on film thickness. The results will be reported elsewhere.

Acknowledgment

References

[1]   H Katayama, S Oda and H Kukimoto *Appl Phys Lett* **27** 697 (1975)

[2]   A Miller, J Staromlynska, I T Munhead, K L Lewis D Graig and G Steward *J Cryst Growth* **86** 859 (1988)

[3]   S Y Wang, I Haukson, J Simpson, H Stewart, S J A Adams, J M Wallace, Y Kawakann, K A Prior and B C Cavenett *Appl. Phys Lett* **61** 506 (1992)

[4]   A Schmidt, M Muller, J Grohs, M Kunz, A Daunois, V Kazukausks, A K Kar, H Bartelt and J Klingshirn *J. Cryst. Growth* **101** 758 (1990)

[5]   A G Milnes and D L Feucht *Heterojunctions and Metal-Semiconductor Junctions* (New York Academic) (1972)

[6]   *File 5-0522, Powder Diffraction File, Set 1-5 (Revised)* (Pennsylvania . Joint Committee on Powder Diffraction Standards) (1974)

[7]   P Scherrer *Gottinger Nachrichten* **2** 98 (1918)

[8]   A L Dawar, P K Shishodia and P C Mathur *J. Mater. Sci Lett* **8** 561 (1989)

[9]   K L Chopra *Thin Film Phenomena* (New York   McGraw Hill) p 270 (1969)

[10]   G Simmons and H Wang *Single Crystal Elastic Constants and Calculated Aggregate Properties   A Handbook* (Massachusetts   M I T Press) p 292 (1971)