Study of Physical Characteristics of Zinc Selenide Thin Film

H N Desai, J M Dhimmar, B P Modi
Department of Physics
Veer Narmad South Gujarat University
Surat-395 007, Gujarat, India

Abstract **- Zinc Selenide (ZnSe) film has been grown on well cleaned glass substrate by thermal evaporation technique under vacuum (5 x 10^{-6} mbar). The physical characteristics of ZnSe film such as compositional, structural and optical properties were examined using energy dispersive X-ray analysis (EDAX), X-ray diffractometer and UV-Visible spectrophotometer respectively. The EDAX study shows that the ZnSe film is almost stoichiometric. Polycrystalline nature of the film was observed from XRD analysis. It is revealed that deposited film has zinc blende system along with some amorphous phase present in ZnSe film and a preferred (3 1 1) orientation. The grain size and lattice strain have been calculated by Williamson-Hall (W-H) plot.Other relevant structural parameters (dislocation density and internal stress) have been calculated. The value of corrected lattice parameter has been determined using Nelson-Riley error function. The optical parameters (optical band gap, Urbach energy and extinction coefficient) have been found for the wavelength region (300 nm -1100 nm) by absorption spectra.**

Keywords- EDAX; XRD; absorption spectra; ZnSe thin film.

I. INTRODUCTION

The group of II –VI compound semiconductors has extensive attention because of their novel properties and many applications. ZnSe has relatively wide band gap, high transparency over wide spectrum range and low value of resistivity which offers an important numbers of optoelectronic applications such as blue and green light emitting diode, LASERs, photodetectors and ultrasonic transducers. It is also applicable for window layer for thin film solar cell [1-4]. ZnSe has either a cubic structure with lattice parameter a = 5.668 Å or hexagonal structure with lattice parameter a = 3.820 Å and c = 6.628 Å [5]. The performance of optoelectronic devices is highly sensitive to the structural properties of the film. Also structural properties such as grain size, lattice constant, crystal phase and orientation depend upon preparation technique and deposition condition [6].

In this paper, ZnSe thin film was prepared by thermal evaporation technique which is easy and conventional method for low costs and large area applications. It is very simple and practicable as compared to other method in industrial production line [7].The physical characteristics of ZnSe film such as compositional, structural and optical properties were studied.

II. EXPERIMENTAL PROCEDURE

The ZnSe film was deposited on well cleaned glass substrate using thermal evaporation technique under vacuum pressure at 5 x 10^{-6} mbar by using HIND HIVAC coating unit (Model: 15F6D). The glass substrate was first cleaned by chromic acid and later on by boiling water and acetone before inserting substrate in the vacuum chamber.The film thickness and deposition rate are 7374 Å and 2-5 Å/s respectively which was measured by quartz crystal monitor.

The quantitative compositional analysis of ZnSe thin film was carried out by energy dispersive X-ray analysis (EDAX). The structural properties of ZnSe film was recorded by X-ray diffractometer (Rigaku, Japan) with Ni-filter CuK$_{\alpha}$ radiation at λ=1.541 Å in the 2θ range 20^{o}-60^{o}. The optical transmittance, absorption and reflectance measurement of the ZnSe film as a function of wavelength was recorded using UV-Visible spectrophotometer (CARY 300, Varian, Australia) in the wavelength range of 300nm - 1100 nm.

III. RESULT AND DISCUSSION

A. Compositional Properties

The chemical composition of the ZnSe film at thickness 7374 Å was determined by energy dispersive x-ray analysis (EDAX) is shown in Fig.1. The peaks of Zn and Se were found which is indicated that the source material is pure and equal proportion. The result of chemical composition of deposited ZnSe thin film is shown in Table 1.

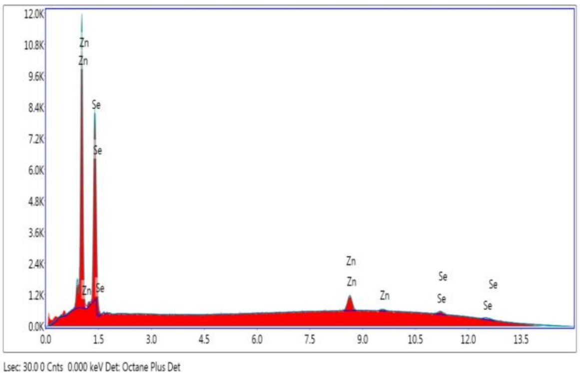

Fig. 1 Energy dispersive x-ray analysis (EDAX) spectrum of ZnSe thin film.

Typical EDAX results shows that the atomic contents percentage of element Zn and Se is found to be 54.4 and 45.6 respectively which showing that the film is almost nearer to stoichiometric. The prepared film had a Se rich composition with an average Zn/ Se weight ratio of 0.99 which is good in agreement with the value obtained from other workers [8, 9]. This is due to the vapour pressure of Se is higher than that of Zn and their sticking coefficient are also different.

TABLE I. WEIGHT AND ATOMIC PERCENT OF SE AND ZN FOR ZNSE THIN FILM.

Element	Weight %	Atomic %	Net Int.	Error %
SeL	50.34	45.63	1,545.4	6.24
ZnK	49.66	54.37	315.6	10.76

B. Structural properties

The structural properties of deposited ZnSe thin film were studied by X-ray diffraction method. The XRD spectra of thermally deposited ZnSe thin film of thickness 7374 Å on the cleaned glass substrate is shown in Fig.2.

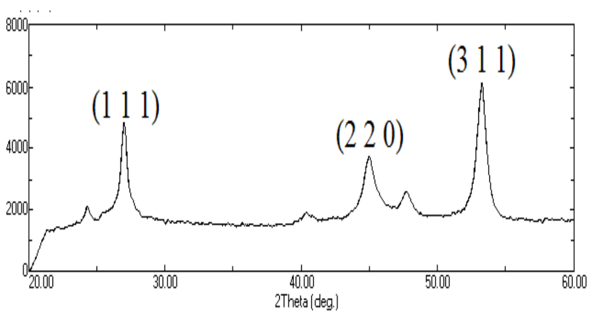

Fig. 2 X- ray diffraction spectra of ZnSe thin film.

The XRD spectra revealed that the film had three peaks at nearly 2θ is equal to 26.98°, 44.96° and 53.24° respectively which correspond to the (1 1 1), (2 2 0) and (3 1 1) reflection which agreed with standard value taken from the JCPDF data file no. 02-0479. Also, it shows that ZnSe film is poly crystalline with cubic zinc blende structure. The other peak observed in XRD pattern due to the amorphous glass substrate and some amorphous present in ZnSe thin film.

TABLE 2. COMPARISON BETWEEN STANDARD D-VALUE AND OBSERVED D-VALUE OF ZNSE THIN FILM

Standard d-value (Å) (JSPDF No.: 02-0479)	Observed d-value (Å)	plane
3.28	3.30	(1 1 1)
2.84	-	(2 0 0)
2.00	2.01	(2 2 0)
1.72	1.72	(3 1 1)
1.41	-	(4 0 0)

The lattice parameter (a) of cubic ZnSe film was calculated by following relation [10];

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

Where h, k and l is miller planes. The value of lattice parameter is found to be 5.701 Å.

The corrected value of lattice parameter is estimated from Nelson-Riley error function [11];

$$f(\theta) = \frac{1}{2}\left[\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right]$$

Where θ is angle of diffraction.

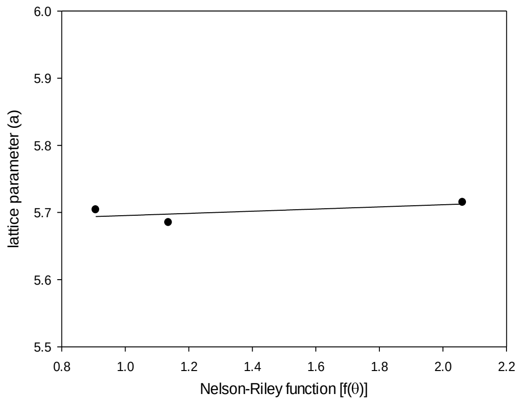

Fig. 3 Nelson-Riley plot for ZnSe thin film

The lattice constant is found to have slightly changed in the values for different orientation of the same film. This is due to source of error in the measurement of 2θ. Nelson-Riley plot for ZnSe thin film have been plotted for different lattice parameter against the error function as shown in Fig. 3. The corrected value of lattice parameter is estimated from the intercept at f(θ)=0. The corrected lattice parameter is 5.679 Å which are closed to bulk ZnSe lattice parameter 5.667 Å (JSPDF No.: 02-0479). However significant change shows that crystallite of film is under strained due to change in nature and concentration of local defects [12].

The entire broadening of diffraction profile is to be due to simultaneous contributions from both particle size (D) and lattice strain (ε) which is calculated by Williamson–Hall method for Cauchy nature of broadened profile [13];

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

Where β is full width at half of the maximum (FWHM) and λ is wavelength of incident X-ray.

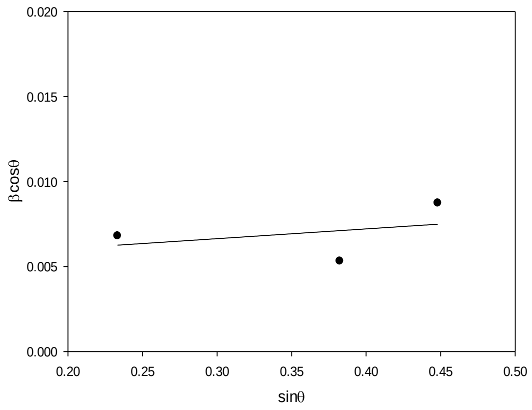

Fig.4 Williamson Hall plot of ZnSe thin film

The Williamson–Hall plot of ZnSe thin film βcosθ versus sinθ is linear in nature as shown in Fig.4. Using the least square fit, the intercept and slope of this plot gives the value of grain size and lattice strain which were found to be 28.67 nm and 1.453 x 10^{-3} respectively.

The average dislocation density (δ) of ZnSe films is found to be 1.34 x 10^{15} m^{-2} by following expression [14];

$$\delta = \frac{15\varepsilon}{aD}$$

Also the average internal stress is defined by [14]
$\sigma = Y\varepsilon$ and it is 0.098 x 10^9 Pa.

Where Y is young modulus of bulk ZnSe (67.2 x 10^9 Pa) [15].

C. Optical Properties

The transmittance and reflectance spectra as a function of wavelength which were determined from absorption spectra by following expression [16];

$$T = \frac{1}{10^A} \quad and \quad A + T + R = 1$$

Where A, T and R is absorption, transmittance and reflectance respectively. The nature of absorption, transmittance and reflectance spectra of ZnSe thin film within the range of 300nm -1100 nm are shown in Fig.5.

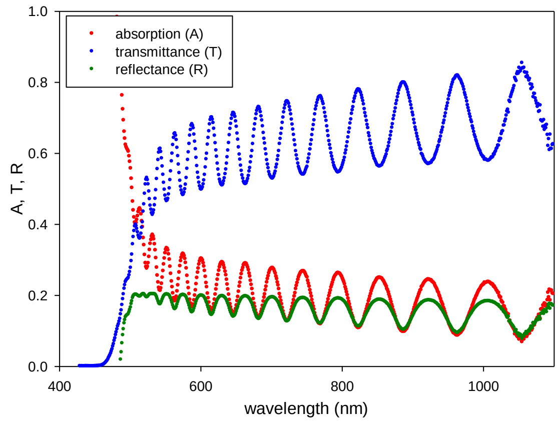

Fig.5 Absorption, transmittance and reflectance spectra as a function of wavelength of ZnSe thin film.

The absorption spectra as a function of wavelength of ZnSe film exhibits sharp absorption edge corresponds to forbidden energy gap. The shape of absorption spectra for ZnSe thin film shows that deposited ZnSe has stoichiometric composition [17, 18]. The transmittance spectra showed a sudden increase in transmittance near to fundamental absorption region. The maximum transmittance is 74% - 84% in wavelength more than 600 nm and a low transmittance in visible region (≤ 500 nm). The transmittance spectra have two main regions: the fundamental absorption region and the interference oscillation region. The nature of transmittance curve is oscillating type indicates that the prepared ZnSe film has good optical quality and homogeneity with uniform thickness [19].

The absorption coefficient (α) can be expressed by following expression;

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

Where A is absorption and t is film thickness.

The value of absorption coefficient is high in order of 10^4 cm^{-1}. Thus, ZnSe film is highly suitable for photo sensors and solar cells. The fundamental absorption edge which corresponds to the direct transition between valance band to conduction band can be used to determine the optical band gap of ZnSe film. The absorption coefficient (α) and photon energy (hυ) was related with Tauc's relation [20];

$$\alpha h\nu = A(E_g - h\nu)^{1/2}$$

Where E_g is optical band gap, A is constant and α is absorption coefficient.

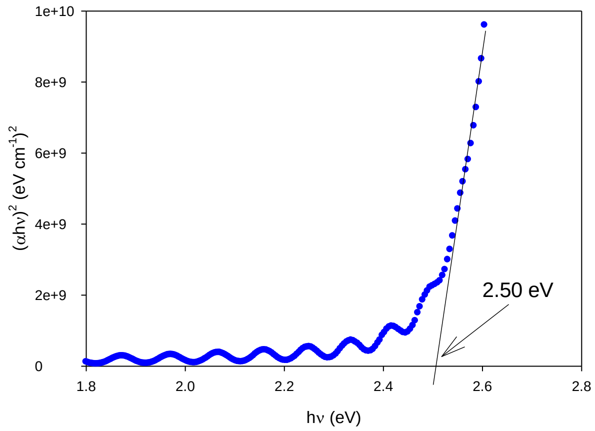

Fig.6 Plot of $(\alpha h\upsilon)^2$ versus hυ of ZnSe thin film.

The plot of $(\alpha h\upsilon)^2$ versus photon energy of ZnSe thin film is shown in Fig.6. The value of optical band gap has been determined by extrapolating the linear portion of the curve to $(\alpha h\upsilon)^2 = 0$. The value of optical band gap of ZnSe thin film is found to be 2.50 eV.

For lower absorption coefficient value, the absorption is depending exponentially on photon energy according to Urbach relation [21];

$$\alpha = \alpha_o \exp\left(\frac{h\nu}{\Delta}\right)$$

Where Δ is Urbach energy.

From the above relation, the Urbach energy was calculated by inverse of slope of the linear part of the curve ln α versus hυ as shown in Fig.7. The Urbach energy was found 130.41 meV. The value of Urbach energy is lower (in order of meV) represented that ZnSe thin film has lower density of localized defect states [22].

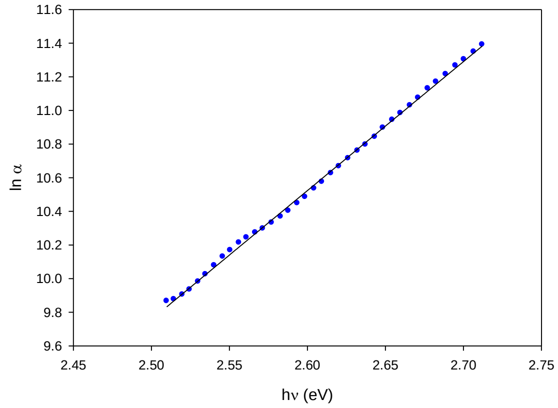

Fig.7 ln α as a function of photon energy of ZnSe thin film.

When electromagnetic radiation is passed through the ZnSe film, a part of energy is lost by absorption and scattering process which is known as extinction coefficient. The extinction coefficient (k) of ZnSe thin film was calculated using following relation [22];

$$k = \frac{\alpha\lambda}{4\pi}$$

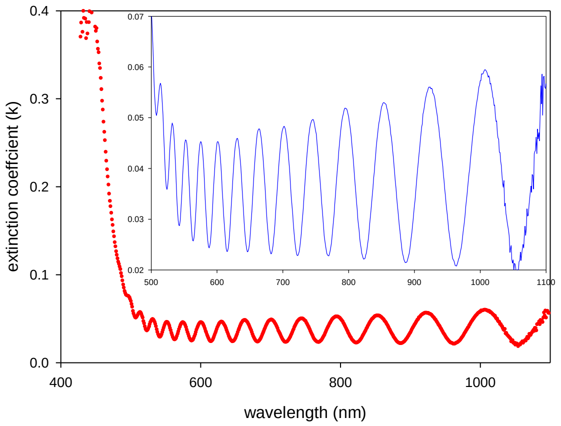

Fig.8 Variation of extinction coefficient as a function of wavelength (range: 400- 1100 nm) [inset: wavelength range 500- 1100 nm]

The variation in the extinction coefficient (k) against wavelength curve is as shown in Fig.8. The lower value of extinction coefficient in visible and infrared region is clearly the indication of excellent surface smoothness of ZnSe thin film [23]. Also, the value of k has higher at strong absorption region due the coupling of electron of ZnSe thin film to the oscillating electric field [24]. The oscillatory behaviour of the extinction coefficient appears due to the variation in the absorbance in grain boundaries [16].

D. Conclusion

The outcome of compositional, structural and optical properties of the thermally deposited ZnSe can be summarised as follows;

From the energy dispersive X-ray analysis (EDAX), the average atomic ratio of Zn and Se is found to be 54.4 and 45.6 respectively and having ratio 1.19 showing that thermally deposited film have purity form and almost stoichiometric.

From X-ray diffraction, it is found that the film is polycrystalline in nature. The lattice parameter and grain size of the film was calculated. The corrected value of lattice constant is found to be 5.679 Å. This due to the lattice misfit of the film with substrate and presence of defects.

From the optical study, it is found that the deposited ZnSe film on glass substrate is highly transparent. The direct optical band gap and Urbach energy were found to be 2.50 eV and 130.41 meV respectively which were obtained from absorption spectra. As the transition is direct wide band gap will be making suitable for window layer for solar cell and optoelectronics devices. The lower value of Urbach energy and extinction coefficient is indicated that ZnSe thin film has good surface smoothness and lower defects.

ACKNOWLEDGMENT

We wish to express to Dr. N. I. Malek, Department of Applied Chemistry, Sardar Vallabhbhai National Institute of Technology (SVNIT), Surat for helping and supporting data acquisition in the work.

REFERENCES

[1] O. Schulz, M. Strassburg, T. Rissom, U. W. Pohl, D. Bimberg, "Post-growth p-type doping enhancement for ZnSe-based lasers using a Li_3N interlayer"Appl. Phys. Lett., Vol. 81, pp. 4916-4918, 2002.

[2] P. Mahawela, G. Sivaraman, S. Jeedigunta, J. Gaduputi, M. Ramalingam, S. Subramanian, "II–VI compounds as the top absorbers in tandem solar cell structures", Mater. Sci. Eng. B, Vol. 116, pp. 283, 2005.

[3] A. Sennaroglu, U. Demirbas, N. Vermeulen, H. Ottevaere, H. Thienpont, "Continuous-wave broadly tunable Cr^{2+}: ZnSe laser pumped by a thulium fiber laser", Opt. Commun., vol. 268, pp. 115-120, 2006.

[4] G. I. Rusu, E. M.Popa, G. G. Rusu, Iulia Salaoru, "On the electronic transport properties of polycrystalline ZnSe films", Appl. Surf. Sci., Vol. 218, pp. 222-230, 2003.

[5] Joint committee on Powder diffraction standards, File no. 9 -387 (1990)

[6] S. Venkatachalam, D. Mangalaraj, Sa. K. Narayandass, K. Kim, J. Yi, "Composition, structural, dielectric and DC characterization of vacuum deposited ZnSe thin films", Vacuum, Vol. 81, pp. 928-933, 2007.

[7] S. H. Kim, H. K. Kim, T. Y. Seong, "Effect of hydrogen peroxide treatment on the characteristics of Pt Schottky contact on n-type ZnO", Appl. Phys. Lett., Vol. 86, pp. 112101, 2005.

[8] C. K. De, N. K. Mishra, T. B. Ghose, "Preparation and structural characterization of ZnSe thin films by X-ray diffraction technique", Indian J. Phys. And Proceeding Of the Indian Association For The Cultivation Of Science A. Vol. 69, pp. 261, 1993.

[9] R. B. Kale, C. D. Lokhande, "Influence of air annealing on the structural, morphological, optical and electrical properties of chemically deposited ZnSe thin films" Appl. Surf. Sci., Vol. 252, pp. 929-938, 2005.

[10] N. Chodhury, B. K. Sharma, "Structural characterization of lead sulfide thin films by means of X-ray line profile analysis", Bull. Mater. Sci., Vol. 32, No.1, pp. 43-47, 2009.

[11] J. B. Nelson, P. D. Riley, "An experimental investigation of extrapolation methods in the derivation of accurate unit-cell dimensions of crystals "Proc. Phys. Soc. London, Vol. 57, pp. 160-177, 1945.

[12] M. Ashraf, S. M. J. Akhtar, A. F. Khan, Z. Ali, A. Qayyum, "Effect of annealing on structural and optoelectronic properties of nanostructured ZnSe thin films", J. of Alloys and Compounds, Vol. 509, pp. 2414-2419, 2011.

[13] Mario Birkholz, Thin Film Analysis by X-ray scattering Wiley – VCH, Weinhein, pp. 123, 2006.

[14] C.K. De, N.K. Mishra, Indian J. Phys., Vol. 71, pp. 530, 1997.

[15] II- VI semiconductor materials and their Application, Edited by Maria C. Tamargo (Taylor and Francis, New York), 2002.

[16] M. Y. Nadeem, Waqas Ahmed, "Optical properties of ZnS thin films",Turk J. Phys., Vol. 24, pp. 651-659, 2000.

[17] J. Krustok, P. E. Kukk, Mater. Sci., Vol. 25, pp. 43, 1989.

[18] P. P. Hankare, P. A. Chate, S. D. Delekar, M. R. Asabe, I. S. Mulla, "Novel chemical synthetic route and characterization of zinc selenide thin films", J. of Phys. And Chem. Of solids, Vol. 67, pp. 2310-2315, 2006.

[19] I. Chambouleyron, J. M. Martinez, A. C. Morelti, M. Mulato, "Retrieval of optical constants and thickness of thin films from transmission spectra" Appl. Opt., Vol. 36, pp. 8238-8247, 1997.

[20] J. Tauc, A. Menth, "States in the gap", J. Non-cryst. Solids, Vol. 8-10, pp. 569-585, 1972.

[21] OmedGh. Abdullah, Bakhtyar K. Aziz, Dler Mohammed Salh, "Structural and optical properties of PVA: $Na_2S_2O_3$ polymer electrolytes films" Indian J. of Appl. Research, Vol. 3, No.11, pp. 477-480, 2013.

[22] H. Howari, "Influence of pulsed laser annealing on the optical properties of thermally evaporated ZnSe thin films", J. of Natural Science and Mathematics, Vol. 5, No. 2, pp. 139-154, 2012.

[23] S. Bhaskar, S. B. Majumder, M. Jain, P. S. Dobal, R. S. Katiyar, "Studies on the structural, microstructural and optical properties of sol–gel derived lead lanthanum titanate thin films", Mat. Sci. And Eng. B, Vol. 57, pp.178, 2001.

[24] V. Gowthami, M. Meenakshi, P. Perumal, R. Sivakumar, C. Sanjeeviraja, "Optical dispersion characterization of NiO thin films prepared by nebulized spray technique", Inter. J. of ChemTech Research, Vol. 6, No. 13, pp. 5169-5202.